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Silver Complexes with 2-Amino-4-Methylpyrimidine: Synthesis, Crystal Structure, and Luminescent Properties

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Abstract—Reactions of $AgReO_4$ and $AgCH_3SO_3$ with L = 2-amino-4-methylpyrimidine (Ampym, $C_5H_7N_3$) in a ratio of 1 : 2 in acetonitrile gave the complexes $[AgL_2(ReO_4)]$ (**I**) and $[AgL_2(CH_3SO_3)]$ (**II**). Their structures were determined. The crystals of complex **I** are monoclinic, space group $C2/c$, a = 5.985(1), b = 3.465(1), c = 19.071(1) Å, β = 96.52(1)°, V = 1527.0(3) Å^3, ρ_{calcd} = 2.507 g/cm^3, Z = 4. The crystals of complex **II** are orthorhombic, space group $Pbca$, a = 14.784(1), b = 11.991(1), c = 17.711(1) Å, V = 3139.7(4) Å^3, ρ_{calcd} = 1.782 g/cm^3, Z = 8. Structure **I** shows discrete cationic complexes $[AgL_2]^+$. The silver atom is virtually linearly coordinated to two N atoms of crystallographically equivalent ligands L (Ag–N, 2.156(4) Å; the angle NAgN, 174.7(4)°). The complex cations are united into zigzag chains through the hydrogen bonds N–H···N. The resulting chains are linked by the hydrogen bonds N–H···O to uncoordinated perrhenate anions to form 2D supramolecular layers. In structure **II**, the Ag^+ ion is coordinated by two crystallographically nonequivalent ligands L in a distorted linear fashion: Ag(1)–N(1), 2.166(7) Å; Ag(1)–N(4), 2.181(6) Å; the angle NAgN, 157.2(2)°. The anions $CH_3SO_3^-$ are weakly linked to the Ag^+ ions (Ag···O 2.72 Å) and are hydrogen-bonded to the complex cations $[AgL_2]^+$, uniting them into supramolecular ribbons.

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INTRODUCTION

Transition metal ions play an important role in the self-assembly of compounds, giving rise to a variety of structural architecture (from discrete to polymeric). In this respect, the silver ion is of special interest because it relates to labile metal centers with the coordination number of Ag^+ from two to six and more. Silver(I) complexes are most commonly obtained from N-containing ligands with various geometries and functional groups. It is known that pyrimidine and its derivatives react with metal ions to give both polynuclear and discrete complexes [1] and participate in hydrogen bonding.

Such ligands as pyrimidine, pyrimidine-2-carbonitrile, and 2-hydroxypyrimidine react wcith Ag^+ and Cu^{2+} ions to form 1D polymer chains through the use of bridging N atoms [1–4]. In some complexes of the formula $M(Dca)_2(Apym)_2$ (M = Co or Ni; Dca is dicyanamide; Apym is 2-aminopyrimidine) [5], pyrimidine derivatives act as monodentate ligands. However, complexes of ZnI_2 with pyrimidine (Pym) may be both discrete ($ZnI_2(Pym)_2$) and polymeric ($ZnI_2(Pym)$), depending on the ZnI_2 : Pym ratio [6]. A study of reactions of Ag^+ ions with Apym and 2-amino-4,6-dimethylpyrimidine (Admpym) [7] has revealed an important role of silver counterions in the formation of coordination polymers of Ag(I) with structures of 1D polymer chains, 2D layers, and 3D supramolecular frameworks.

In this work, we describe the synthesis, structures, and luminescent properties of two complexes $[AgL_2(ReO_4)]$ (**I**) and $[AgL_2(CH_3SO_3)]$ (**II**), where L is 2-amino-4-methylpyrimidine (Ampym).

EXPERIMENTAL

Synthesis of complexes I and II. The starting reagents $AgCH_3SO_3$ and L were purchased from Aldrich; $AgReO_4$ was prepared from $AgNO_3$ and NH_4ReO_4 [8]. For the synthesis of complex **I**, $AgReO_4$ (0.39 g, 1.09 mmol) and ligand L (0.23 g, 2.11 mmol) were separately dissolved in acetonitrile (6 mL). Then the solutions were mixed with stirring and the resulting reaction mixture was kept in the dark at room temperature. The crystals that formed were washed with a small amount of acetonitrile, dried in air, and examined by elemental analysis. Single crystals suitable for X-ray diffraction were obtained by recrystallization from acetonitrile–NH_4OH.

For $C_{10}H_{14}N_6O_4AgRe$

anal. calcd. (%):	N, 13.76;	C, 20.90;	H, 2.33.
Found (%):	N, 14.57;	C, 20.82;	H, 2.43.

For the synthesis of a methanesulfonate complex with $Ag(CH_3SO_3)$: L = 1 : 2, $AgCH_3SO_3$ (0.20 g, 1.0 mmol) and ligand L (0.22 g, 2.02 mmol) were dis-

Table 1. Crystallographic parameters and the data collection and refinement statistics for structures **I** and **II**

Parameter	Value	
	I	**II**
M	576.34	421.24
Crystal dimensions, mm	0.25 × 0.15 × 0.08	0.45 × 0.25 × 0.10
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$Pbca$
Unit cell parameters:		
a, Å	5.985(1)	14.784(1)
b, Å	13.465(1)	11.991(1)
c, Å	19.071(1)	17.711(1)
β, deg	96.52(1)	90
V, Å^3	1527.0(3)	3139.7(4)
Z, ρ_{calcd}, g/cm^3	4, 2.507	8, 1.782
μ_{Mo}, mm^{-1}	9.229	1.438
$F(000)$	1080	1696
Temperature, K	293	
Radiation (l, Å)	MoK_α (0.71073), graphite monochromator	
Scan mode	ω	
θ Scan range, deg	3.03–31.96	2.47–27.97
Ranges of h, k, and l indices	$-1 \le h \le 8$, $-1 \le k \le 20$, $-28 \le l \le 28$	$-1 \le h \le 19$, $-1 \le k \le 15$, $-23 \le l \le 2$
Number of measured reflections	3544	4924
Number of reflections with $I \ge 2\sigma(I)$	2638	3745
R_{int}	0.0277	0.0839
Number of parameters refined	102	200
GOOF on F^2	0.790	0.816
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0292$, $wR_2 = 0.0838$	$R_1 = 0.0391$, $wR_2 = 0.1015$
R (for all reflections)	$R_1 = 0.0743$, $wR_2 = 0.1109$	$R_1 = 0.2487$, $wR_2 = 0.1860$
Molar absorption coefficient	0.00041(17)	0.0010(3)
Residual electron density (max/min), e/Å^3	1.017/–2.180	0.655/–0.695

solved with stirring in acetonitrile (20 mL). Then ethanol (5 mL) was added and the reaction mixture was filtered. After 1 h, the fine crystalline fraction that formed was separated from the solution. The mother liquor was kept in the dark under the conditions that ensured slow evaporation of the solvents. After 48 h, the thin prismatic crystals that formed were filtered off, washed with a small amount of acetonitrile, and dried in air. According to elemental analysis data, the crystals correspond to the formula [$AgL_2(CH_3SO_3)$] (**II**).

For $C_{11}H_{17}N_6O_3SAg$

anal. calcd. (%):	N, 19.95;	C, 31.37;	H, 4.07;	S, 7.60.
Found (%):	N, 19.69;	C, 31.36;	H, 3.91;	S, 7.99.

The IR spectra of ligand L and complexes **I** and **II** were recorded on a Specord 75 IR spectrometer (KBr) in the 4000–400 cm^{-1} range using a standard procedure for sample preparation with Vaseline.

X-ray diffraction study. Experimental reflection intensity data for the single crystals of complexes **I** and **II** were collected on an Enraf-Nonius CAD4 automated diffractometer. The structures were solved by the direct methods (SHELXS-97) [9] and refined by the least-squares method in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [10]. The hydrogen atoms were located geometrically and refined using a riding model with fixed isotropic thermal parameters. The H atoms of water molecules were located in difference electron-density maps.

Selected crystallographic parameters and the data collection and refinement statistics for structures **I** and **II** are summarized in Table 1. The geometrical parameters of the hydrogen bonds are given in Table 2. Comprehensive structural data have been deposited with the Cambridge Crystallographic Data Centre (nos. 914737 (**II**) and 914738 (**I**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 2. Geometrical parameters of the hydrogen bonds in structure **I**

Hydrogen bond D–H···A	Distance, Å			Angle DHA, deg	Coordinates of the atom A
	D···A	D–H	H···A		
			I		
N(2)–H(2a)···N(3)	3.030(6)	0.86	2.18	172	$-x, -y + 1, -z$
N(2)–H(2b)···O(1)	2.846(6)	0.86	2.01	165	$x - 1/2, y - 1/2, z$
			II		
N(5)–H(5d)···O(1)	2.962(7)	0.86	2.110	173	$-x + 1/2, y + 1/2, z$
N(5)–H(5e)···O(3)	2.822(6)	0.86	2.09	174	x, y, z
N(2)–H(2b)···O(3)	2.947(6)	0.86	2.46	144	$-x + 1/2, y - 1/2, z$
N(2)–H(2c)···(O2)	2.976(6)	0.86	2.14	164	x, y, z

Emission spectra were recorded on an LS55 spectrometer (PerkinElmer) in the 200–900 nm range at room temperature (resolution 0.5 nm, slit width varied from 3 to 5 nm); an attachment for measuring luminescence of solids was used.

Electronic absorption spectra were recorded in standard quartz cells for liquid samples on a Cary5000 UV-Vis spectrophotometer in the 175–3300 nm range (resolution 0.05 nm).

RESULTS AND DISCUSSION

The IR spectrum of complex **I** shows an intense absorption band at 890 cm^{-1} (ν(Re–O)). The spectra of both complexes **I** and **II** exhibit two very strong absorption bands at 1138 and 1166 cm^{-1} for **I** and at 1113 and 1195 cm^{-1} for **II**, which are absent from the IR spectrum of free ligand L. For this reason, we assigned them to the ν(S–O) stretching vibrations in the anion $CH_3SO_3^-$ [11].

In the spectra of complexes **I** and **II**, the positions of the bands due to the antisymmetrical and symmetrical ν(N–H) stretching vibrations of the NH_2 group of the coordinated ligand L differ only slightly from those for the free ligand (3290 and 3195 cm^{-1}). Earlier, in the study of silver complexes with aniline derivatives (e.g., $[Ag(C_{24}H_{28}N_2)_{1.5}]NO_3$ [12]), we have found that the ν(N–H) bands of a coordinated NH_2 group are substantially shifted to the lower frequencies from their positions in the spectrum of free molecule L. The spectra of complexes **I** and **II** suggest that Ampym is coordinated to the metal center only through the N atoms of the heterocycle.

Structure **I** shows discrete cationic complexes $[AgL_2]^+$. The Ag^+ ion is on the axis 2 and virtually linearly coordinated to two N atoms of crystallographically equivalent ligands L (Ag–N, 2.156(4) Å; the angle NAgN, 174.7(4)°). The planes of the rings N_2C_4 of the coordinated ligands L make a dihedral angle of 85.5°. The complex cations $[AgL_2]^+$ are united through the hydrogen bonds N–H···N into supramolecular zigzag chains $[AgL_2]^+_\infty$, along the direction [001]. A fragment of structure **I** with supramolecular chains is shown in Fig. 1. The anions $[ReO_4]^-$ (Re–O 1.679(7)–1.692(5) Å; the angles OReO, 105.5°–110.9°) act as proton acceptors in the hydrogen bonds N–H···O that unite the chains into 2D supramolecular layers along the direction [010] through 1/2*b* (Fig. 2; Table 2). In structure **II**, the Ag^+ ion is coordinated by two crystallographically nonequivalent ligands L in a distorted linear fashion: Ag(1)–N(1), 2.166(7) Å; Ag(1)–N(1), 2.181(6) Å; the angle NAgN, 157.2(2)° (Fig. 3). The Ag^+ ion is weakly linked to the methanesulfonate anion $CH_3SO_3^-$ (Ag···O 2.72 Å). The nonlinear geometry of complex **II** is probably due to the weak interaction of the Ag^+ ion with the methanesulfonate anion. The dihedral angle between the planes of the adjacent pyrimidine rings is 73.8°. The complexes $[AgL_2]^+$ are united through the hydrogen bonds N–H···O (with the anions $CH_3SO_3^-$ as proton acceptors) into supramolecular ribbons running along

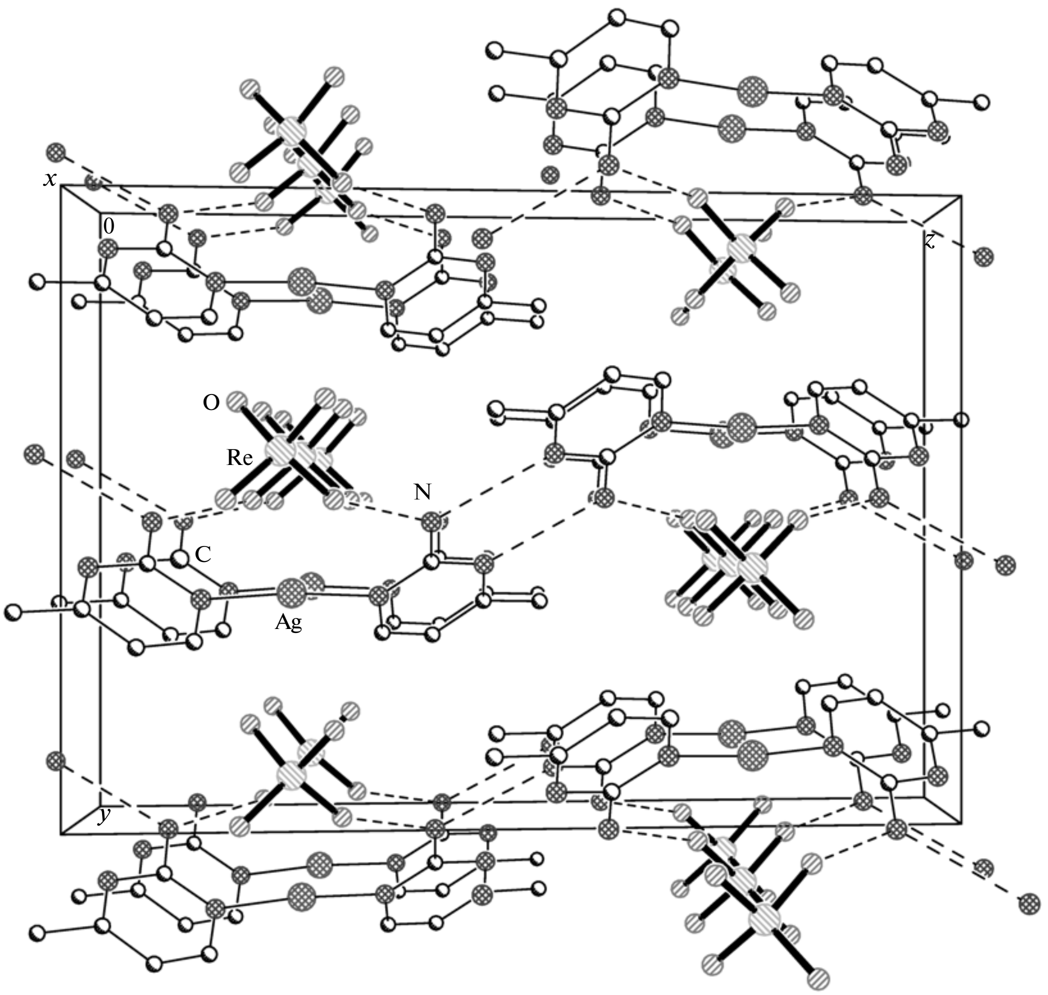

Fig. 1. Crystal packing of structure **I** along the direction [100], with the hydrogen bonds forming supramolecular chains.

the direction [010] (Fig. 3, Table 2). One of the ribbons in Fig. 3 is set in bold for clarity.

The electronic absorption spectra of free ligand L and complexes **I** and **II** are shown in Fig. 4. The spectra of their solutions were recorded at room temperature. It can be seen in Fig. 4 that the spectra are virtually identical. The spectral patterns for complexes **I** and **II** are slightly shifted (by ~8 nm) to the shorter wavelengths compared to that of free ligand L. In addition, the absorption bands at 200–300 nm in the spectrum of complex **II** are resolved better than those for free ligand L and complex **I**. These bands can be assigned to the transitions $\pi \rightarrow \pi^*$ within the ligand molecule. This is supported by the nearly equal intensities of the absorption bands for free ligand L and complexes **I** and **II** (in all measurements, the concentration of the solutions was the same); i.e., the absorption is due to the electronic transitions in ligand L. The variation of the metal center does not affect these processes appreciably.

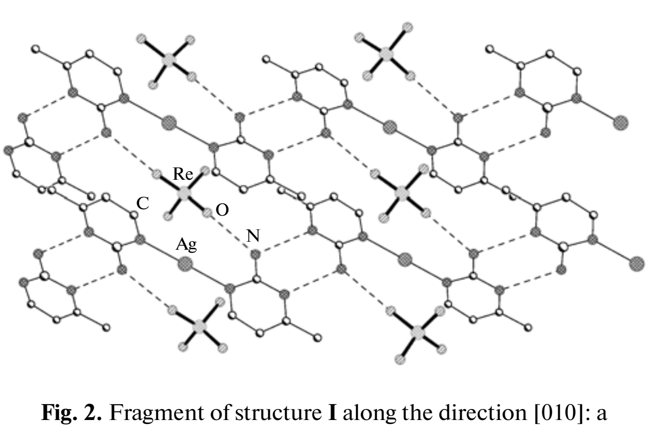

Fig. 2. Fragment of structure **I** along the direction [010]: a 2D supramolecular layer made up of anion-bonded chains.

The room-temperature emission spectra (visible region) of solid samples of L, **I**, and **II** irradiated with UV light are shown in Fig. 5. All three compounds are characterized by blue luminescence; the spectral pattern for these compounds remains virtually unchanged. The most intense emission bands for free ligand L appear at 366 and 422 nm; their intensities are

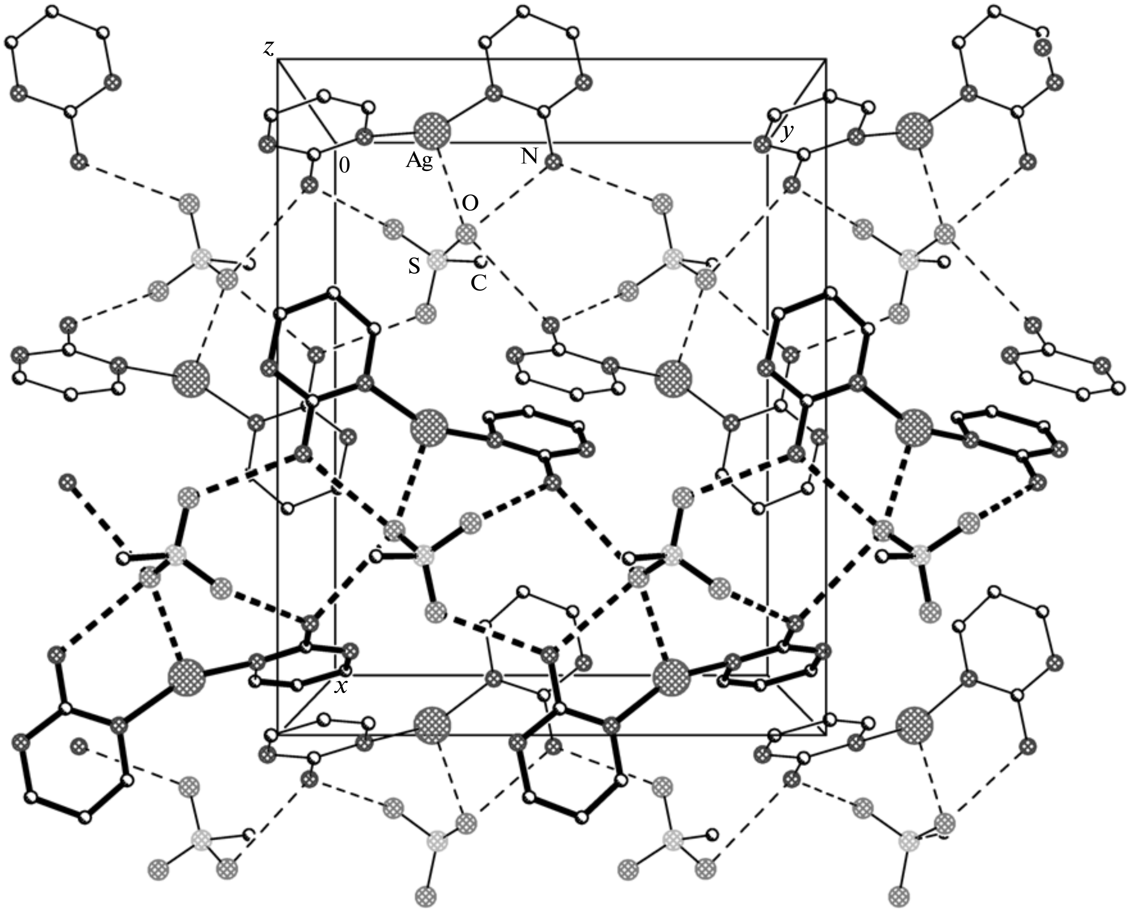

Fig. 3. General view of structure **II** with supramolecular ribbons.

nearly equal. The emission spectrum of complex **I** is similar; however, the peak at 422 nm is substantially weaker than the peak at 366 nm. Some changes are observed in the spectrum of complex **II**. The most intense peak at 400 nm is much stronger than the peak at 366 nm. The relative intensities of the peaks at 483 and 528 nm remain virtually unchanged for all three compounds. One can believe that the emission of complexes **I** and **II** are largely due to the transitions $\pi \rightarrow \pi^*$ in ligand L and probably the metal ions produce no appreciable sensitizing effect in this case.

To sum up, we found that structures **I** and **II** are made up of discrete complexes with a Ag : L ratio of 1 : 2. Note that both $AgReO_4$ and $Ag(CH_3SO_3)$ react with 2-amino-4-methylpyrimidine to give only complexes **I** and **II**, respectively; the outcome of the reaction is independent of whether an equimolar ratio of the reactants or a twofold excess of the ligand in acetonitrile has been used. Smith et al. have demonstrated that reactions of silver *p*-tosylate with 2-aminopyrimidine and 2-amino-4,6-dimethylpyrimidine in alcoholic media produce complexes with Ag : Apym = 1 : 1 and Ag : Admpym = 2 : 3 [13]. These pyrimidine derivatives act as bridging ligands. In all these syntheses, the presence of the NH_2 group in the ligands favors the formation of strong hydrogen bonds N—H···O(N) that stabilize a supramolecular architecture.

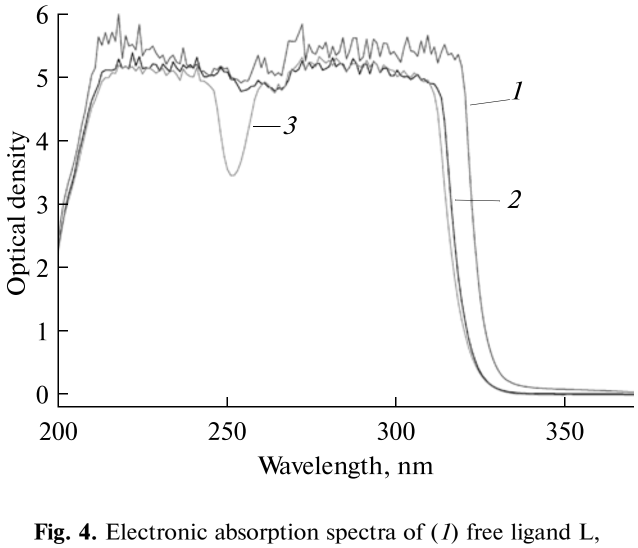

Fig. 4. Electronic absorption spectra of (*1*) free ligand L, (*2*) complex **I**, and (*3*) complex **II**.

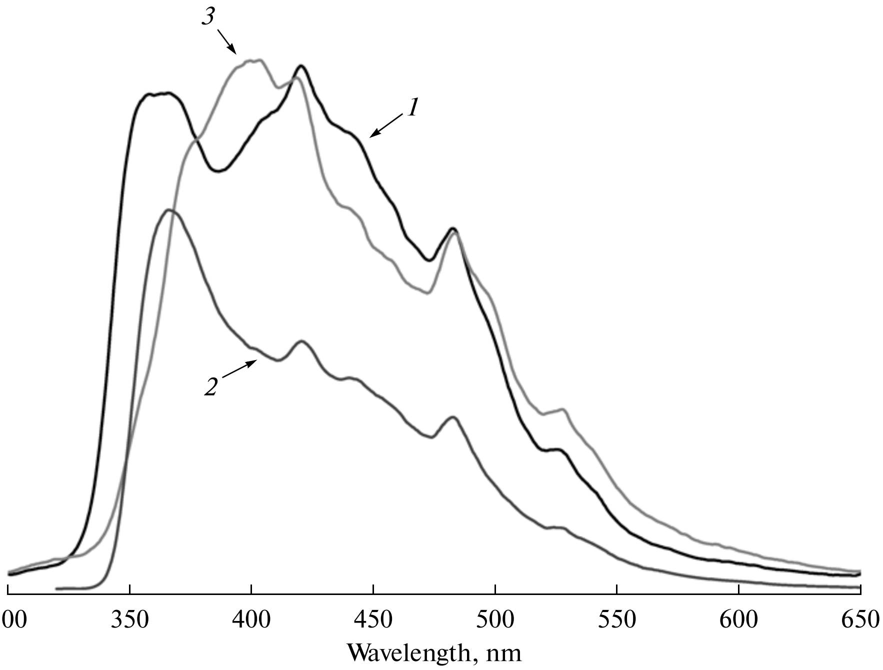

Fig. 5. Emission spectra of (*1*) free ligand L (λ_{ex} = 256 nm), (*2*) complex **I** (λ_{ex} = 282 nm), and (*3*) complex **II** (λ_{ex} = 294 nm).

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REFERENCES

1. Navarro, J.A.R., Barea, E., Galindo, M.A., et al., *J. Solid State Chem.*, 2005, vol. 178, p. 2436.
2. Krishnamohan Sharma, C.V., Griffin, S.T., and Rogers, R.D., *J. Chem. Soc., Chem. Commun.*, 1998, p. 215.
3. Kokunov, Yu.V. and Gorbunova, Yu.E., *Russ. J. Inorg. Chem.*, 2007, vol. 52, no. 10, p. 1530.
4. Tabares, L.S., Navarro, J.A.R., Salas, J.M., and Willermann, M., *Inorg. Chim. Acta*, 2001, vol. 318, nos. 1–2, p. 166.
5. Jensen, P., Batten, S.R., Monbaraki, B., and Murray, K.C., *J. Chem. Soc., Chem. Commun.*, 2000, p. 793.
6. Nather, C., Bhosekar, G., and Jess, I., *Inorg. Chem.,* 2007, vol. 46, no. 19, p. 8079.
7. Wang, Y.-H., Chu, K.-L., Chen, H.-C., et al., *CrystEngComm,* 2006, vol. 8, p. 84.
8. Kokunov, Yu.V., Gorbunova, Yu.E., and Kovalev, V.V., *Russ. J. Coord. Chem.*, 2012, vol. 38, no. 4, p. 245.
9. Sheldrick, G.M., *SHELXS-97. Program for the Solution of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
10. Sheldrick, G.M., *SHELXL-97. Program for the Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
11. Bellamy, L.J., *The Infrared Spectra of Complex Molecules*, New York: Wiley, 1958.
12. Kokunov, Yu.V., Gorbunova, Yu.E., and Kovalev, V.V., *Russ. J. Inorg. Chem.*, 2012, vol. 57, no. 7, p. 953.
13. Smith, G., Clout, B.A., Lynch, D.E., et al., *Inorg. Chem.,* 1998, vol. 37, p. 3236.

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