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Coordination Compounds of Silver Methanesulfonate with Triphenylphosphine and 1,2-Bis(4-Pyridyl)ethane

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Abstract—The reaction of $Ag(CH_3SO_3)$ with PPh_3 gave the compound $[Ag(CH_3SO_3)(PPh_3)_2]$ (**I**) and the reaction of $Ag(CH_3SO_3)$ with PPh_3 and 1,2-bis(4-pyridyl)ethane (Dpe) affords the mixed complex $[Ag(CH_3SO_3)(PPh_3)(Dpe)]$ (**II**). The crystal structures of **I** and **II** were determined by X-ray diffraction (CIF file CCDC no. 1563357 (for **I**)). In **I**, the centrosymmetric binuclear complex $[Ag(CH_3SO_3)(PPh_3)_2]_2$ is formed. The Ag atom has a distorted tetrahedral coordination composed of two bidentate bridging O atoms of the sulfonate anion and two P atoms of two PPh_3 ligands. The structure of **II** is based on the centrosymmetric binuclear molecule with two bridging Dpe ligands between two $[Ag(CH_3SO_3)(PPh_3)]$ complexes. The O atoms of the methanesulfonate ion are statistically disordered, which induces a considerable distortion of the silver polyhedron with C.N. 5. Both compounds tend to emit in the blue and green regions of the PL spectra.

Keywords: coordination compounds of silver methanesulfonate, bridging 1,2-bis(4-pyridyl)ethane ligand, structure, luminescence properties

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INTRODUCTION

Most of silver sulfonates possess 2D or 3D polymer structures [1–4]. The silver ion preferably coordinates soft bases such as P-containing ligands. The coordination of tertiary phosphines to the silver ion has been thoroughly studied [5]. However, complexes of silver sulfonates with PPh3 are few in number. Silver complexes with Lewis bases attract increased attention, most of all, since they are used as precursors for the fabrication of thin silver films [6, 7]. The phosphines PR3 play an important role in the coordination chemistry. Owing to their versatile character, they not only stabilize the low oxidation state of metals, but can also be coordinated to metal atoms in higher oxidation states. Phosphine ligands determine the properties of the excited states of coordination compounds. Phosphines directly participate in the charge transfer as they are able to exhibit donor and acceptor properties [8].

Currently, several triphenylphosphine silver complexes with carboxylate and sulfonate anions are known. Depending on the PPh_3 : Ag ratio and the solvent, monomeric, dimeric, trimeric, or tetrameric complexes with C.N.(Ag) of 3 and 4 are formed. Examples of carboxylate silver complexes with PPh_3 are provided by $Ag(CH_3CO_2)(PPh_3)_2$, $Ag_2(CH_3CO_2)_2(PPh_3)_2 \cdot H_2O$ [9], and $Ag(CF_3CO_2)(PPh_3)_2$ [10] and the trifluoromethanesulfonates $Ag(CF_3SO_3)$-$(PPh_3)_2$, $[Ag(CF_3SO_3)(PPh_3)]$ [11], and $[Ag_3(CF_3SO_3)_3$- $(PPh_3)_3]$ [12]. Published data are available for the structures of two silver methanesulfonate complexes with triphenylphosphine, $[Ag(CH_3SO_3)(PPh_3)]_4 \cdot 4CH_2Cl_2$ and $[Ag(CH_3SO_3)(PPh_3)_2] \cdot CH_2Cl_2$ [6], containing dichloromethane solvate molecules in the crystal lattice. Compounds of silver sulfonates simultaneously containing phosphine and other electron-donating ligands in the coordination sphere are rather rarely encountered. The structures are known for $[Ag(C_6H_4\text{-}4\text{-}Me)SO_3(PPh_3)(EtOH)]$, with the EtOH molecule being incorporated in the Ag^+ coordination sphere [13], and for $[Ag_2L(PPh_3)_4(H_2O)] \cdot 1.5\ MeCN \cdot 0.5\ H_2O$ (L = 3-carboxylate-4-hydroxybenzosulfonate) [14], in which only a water molecule is present in the Ag coordination sphere apart from the sulfonate and phosphine ligands. To our knowledge, no mixed coordination compounds of silver sulfonates containing simultaneously phosphine and an N-ligand have been reported. However, mixed silver compounds containing halide ions, phosphine, and pyridine are known, in particular, $[Ag_2I_2Py_2\{P(n\text{-}Tol_3\}_2]$ [15], $AgClPy(PPh_3)$ and $AgBrPy(PPh_3)_2$ [16] (with the Ag–N coordination bond), and $[Ag_2Cl_2(PPh_3)_2$(2-aminopyrimidine$)_2]$ (with a 2-aminopyrimidine bridge) [17]. Mixed compounds based on AgX (X = NO_3, ClO_4, CH_3COO, CF_3COO) with phosphine and N-containing aromatic ligands have been obtained and their structures have been determined [18–20].

In this study, we prepared two mixed coordination compounds, namely, $[Ag(CH_3SO_3)(PPh_3)_2]$ (**I**) without solvate molecules and $[Ag(CH_3SO_3)(PPh_3)(Dpe)]$ (**II**) (Dpe = 1,2-bis(4-pyridyl)ethane), and studied their structures and photoluminescence spectra.

EXPERIMENTAL

Commercial $AgCH_3SO_3$ and Dpe (Aldrich) and reagent grade PPh_3 were used.

Synthesis. Dry PPh_3 (0.40 g, 1.54 mmol) was added with stirring to a solution of $Ag(CH_3SO_3)$ (0.16 g, 0.77 mmol) in 10 mL of acetonitrile preheated to 30–40°C and, after dissolution of the phosphine, a solution of Dpe (0.14 g, 0.76 mmol) in 4 mL of acetonitrile was added. The solution thus formed was kept for an hour in a closed vessel at room temperature and filtered; the filtrate was left for 2 days in the dark for slow evaporation of the solvent. The large prismatic crystals thus formed were separated by decantation and, without washing, dried in air. According to chemical analysis, the crystals of **II** corresponded to a mixed-ligand silver complex of the composition $[Ag(CH_3SO_3)(PPh_3)(Dpe)]$.

For $C_{31}H_{30}N_2O_3PSAg$

Anal. calcd., %	N, 4.32	C, 57.40	H, 4.66	S, 4.93
Found, %	N, 3.91	C, 57.21	H, 4.85	S, 3.58

The mother liquor after the separation of the crystals of **II** was kept for 24 h to give much smaller-sized crystals, which were separated from the solution, dried, and analyzed. According to elemental analysis, the crystals of **I** had the composition $[Ag(CH_3SO_3)(PPh_3)_2]$.

For $C_{37}H_{33}O_3P_2SAg$

Anal. calcd., %	C, 61.15	H, 4.58	S, 4.40
Found, %	C, 59.54	H, 4.66	S, 3.69

X-ray diffraction. The experimental reflections for the crystals of **I** and **II** were collected on a CAD-4 Enraf-Nonius automated diffractometer. In both cases, the structure was solved by the direct methods (SHELXL-97) [21] and refined by least squares in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [22]. The positions of hydrogen atoms were calculated geometrically and included in the refinement according to the riding model. The crystals of **II** are prone to twinning, which reduces the accuracy of the experiment and requires growing new crystals and structure refinement.

The key crystallographic data and X-ray experiment details for structures **I** and **II** are summarized in Table 1. The full crystallographic characteristics for **I** are deposited with the Cambridge Crystallographic Data Centre (no. 1563357, http://www.ccdc.cam.ac.uk/serices/structure_deposit/).

Photoluminescence (PL) spectra were measured at room temperature on an PE LS-55 spectrometer (0.5 nm resolution; the slits were varied in the 7–10 nm range; the attachment for solid-state samples was used; emission spectra were constructed taking account of the instrumental error).

RESULTS AND DISCUSSION

The centrosymmetric binuclear complex, $[Ag(CH_3SO_3)(PPh_3)_2]_2$, is formed in **I** (Fig. 1). The Ag(1)···Ag(1*A*) distance is 5.41 Å. The Ag^+ ion, coordinated by two phosphorus atoms of two triphenylphosphine ligands and by two oxygen atoms of two crystallographically equivalent methanesulfonate anions, has a distorted tetrahedral coordination (distances: Ag(1)–P(1), 2.458(1); Ag(1)–P(2), 2.439(1); Ag(1)–O(1), 2.313(4); Ag(1)–O(2*A*), 2.513(4) Å; angles: O(1)Ag(1)P(2), 117.5(2)°; O(1)Ag(1)P(1), 108.7(1)°; P(2)Ag(1)P(1), 126.27(4)°; O(1)Ag(1)O(2*A*), 95.5(2)°; P(2)Ag(1)O(2*A*), 97.5(1)°; P(1)Ag(1)O(2*A*), 104.1(1)°). In **I**, the P–C(aver.) distances (1.821(5) Å) for two independent PPh_3 ligands are consistent with those in the isostructural compound $[Ag(CF_3SO_3)\text{-}(PPh_3)_2]$ [11] and in some other silver compounds containing triphenylphosphine ligands [6, 12]. The nonspecific C–H···O hydrogen bonds are summarized in Table 2.

Binuclear complex **I** contains the $[Ag_2O_4]$ metallacycle; the methanesulfonate anions function as bidentate bridges between the two Ag atoms. The O(3) oxygen atom is not involved in the coordination of silver. The distances in the $CH_3SO_3^-$ ion are as follows: S(1)–O(1), 1.401(4); S(1)–O(2), 1.413(4); S(1)–O(3), 1.450(6); and S(1)–C(1), 1.700(7) Å.

Compound **II** is a centrosymmetric binuclear molecule with two Dpe bridging ligands between two $[Ag(CH_3SO_3)(PPh_3)]$ complexes (Fig. 2). The oxygen atoms of the methanesulfonate group are statistically disordered, each over two sites with occupancies of 0.633 and 0.367. As can be seen in Fig. 2, only one oxygen atom in each site is incorporated, together with the P and N atoms of organic ligands, into the Ag^+ coordination sphere (Ag(1)–O(1), 2.39(2); Ag(1)–O(5), 2.45(3); Ag(1)–P(1), 2.367(3); Ag(1)–N(1), 2.384(10) Å). Apparently, this orientation of the methanesulfonate ion induces a considerable distortion of the silver polyhedron with C.N. 5. The minimum angle at Ag(1) between the statistically disordered oxygen atoms is unrealistically small: O(1)Ag(1)O(5), 36.0(8)°. The other angles vary over a broad range: 80.1(8)°–126.6(8)°. Because of the disorder of the

Table 1. Crystallographic data and key experiment details for structures **I** and **II**

Parameter	Value	
	I	**II**
Molecular formula	$C_{37}H_{33}O_3P_2SAg$	$C_{31}H_{30}N_2O_3PSAg$
M	727.50	649.47
System	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.350(1)	9.014(1)
b, Å	12.518(1)	9.662(1)
c, Å	13.315(1)	16.975(1)
α, deg	90.14(1)	85.98(1)
β, deg	117.26(1)	79.76(1)
γ, deg	110.29(1)	89.28(1)
V, Å^3	1684.0(3)	1451.3(2)
Z	2	2
ρ(calcd.), g/cm^3	1.435	1.486
μ_{Mo}, mm^{-1}	0.790	0.856
F(000)	744	664
Color, habit	Colorless block	Colorless block
Crystal size, mm	0.18 × 0.13 × 0.08	0.20 × 0.18 × 0.10
T, K	293(2)	293(2)
Radiation (λ, Å)	MoK_α (0.71073), graphite monochromator	MoK_α (0.71073), graphite monochromator
Scan mode	ω	ω
Range of θ, deg	2.02–27.97	2.11–26.00
Index ranges	$-16 \le h \le 1$, $-15 \le k \le 16$, $-16 \le l \le 17$	$-1 \le h \le 11$, $-11 \le k \le 11$, $-20 \le l \le 20$
Number of reflections measured/independent (R_{int})	9085/7988 (0.0415)	6784/5669 (0.0412)
Number of reflections with $I \ge 2\sigma(I)$	3726	809
Completeness on θ = 27.97° (**I**), 26.00° (**II**), %	98.5	99.2
Absorption correction	Semiempirical from equivalents	Semiempirical from equivalents
T_{min}/T_{max}	0.8708/0.9395	0.8474/0.9193
Number of refined parameters	397	245
GOOF on F^2	0.970	1.238
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0432$, $wR_2 = 0.1127$	$R_1 = 0.1079$, $wR_2 = 0.2988$
R (all data)	$R_1 = 0.1582$, $wR_2 = 0.1482$	$R_1 = 0.2052$, $wR_2 = 0.3478$
Residual electron density, (max/min), e/Å^3	1.498/–0.920	2.423/–1.241
Extinction coefficient		0.010(4)

Table 2. Geometric parameters of hydrogen bonds in structures **I** and **II**

D–H···A	Distance, Å			DHA angle, deg	Coordinates of A atom
	D···A	D–H	H···A		
C(7)–H(7*A*)···O(2)	3.315(7)	0.93	2.69	126	$-x + 1, -y + 1, -z + 1$
C(10)–H(10*A*)···O(3)	3.345(8)	0.93	2.67	130	$-x + 1, -y + 2, -z + 1$
C(24)–H(24*A*)···O(1)	3.395(7)	0.93	2.76	125	$-x + 1, -y + 2, -z + 1$

methanesulfonate anion, the C–H···O hydrogen bond has not been studied.

As noted above, compound **I** has a dimeric structure and the Ag^+ ion has a distorted tetrahedral coordination. Analysis of the structural data for silver phosphine sulfonate coordination compounds indicates that this is a rather widely encountered structural type for the $[AgX(PPh_3)_2]$ complexes ($[Ag(NO_3)(PPh_3)_2]$ [23], $[AgCl(PPh_3)_2]$ [24], [AgI(*p*-Tol_3)Py] [14], $[Ag(CF_3SO_3)(PPh_3)_2]$ [25]). However, the complexes $[Ag(CF_3CO_2)(PPh_3)_2]$ [10] and $[Ag(NO_2)(PPh_3)_2]$ CH_2Cl_2 [26] are monomeric.

In the dimers, each silver atom is linked to two PPh_3 ligands and two oxygen atoms of different triflate ions. A decrease in the Ag : PPh_3 ratio to 1 : 1 is accompanied by the formation of trinuclear compounds [11, 12]. It has been found [18–20] that the reactions of AgX (X = NO_3^-, ClO_4^-, CF_3COO^-, CH_3COO^-) with PPh_3 and N-containing aromatic ligands (2,2-Bipy,

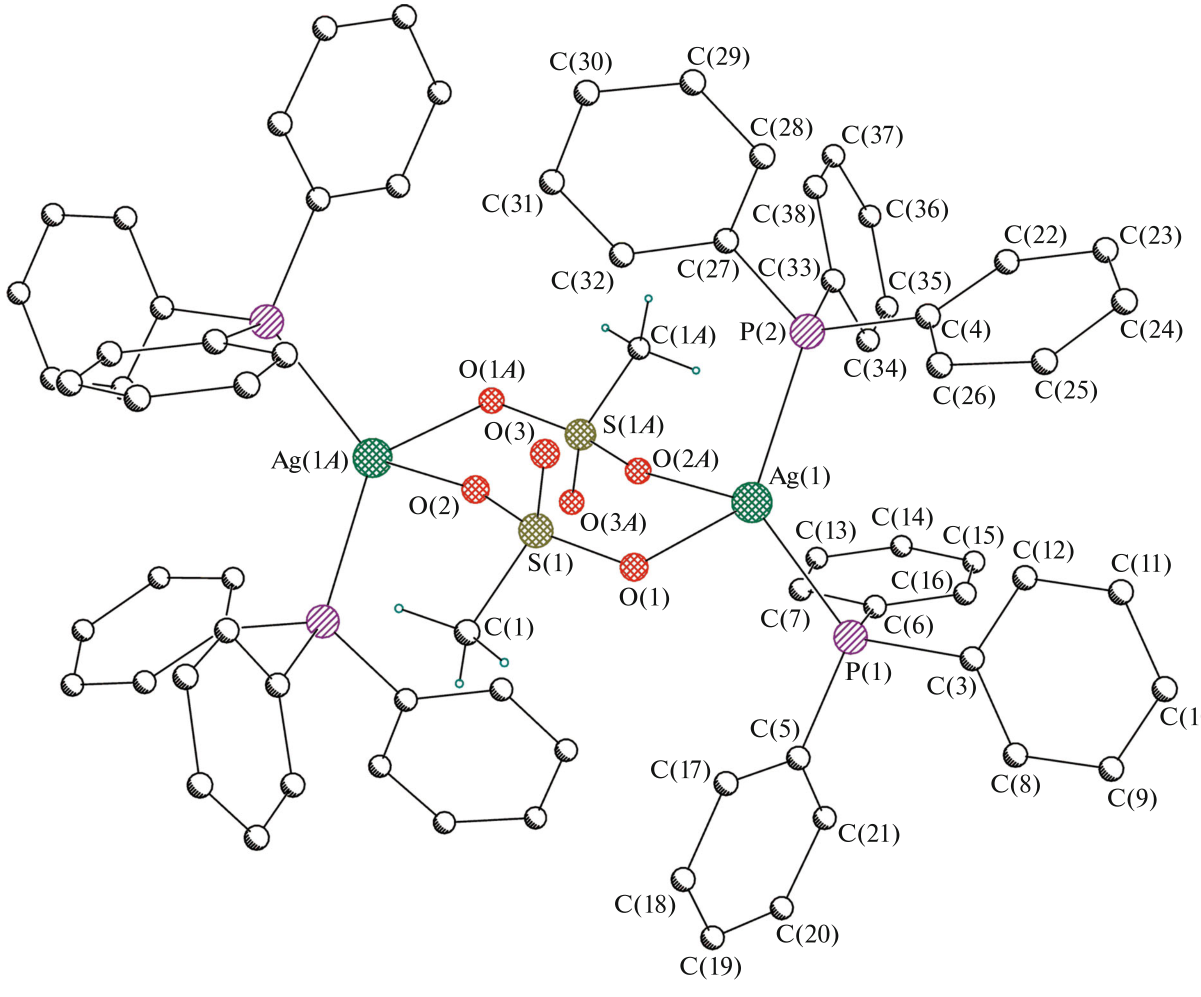

Fig. 1. Binuclear complex $[Ag(CH_3SO_3)(PPh_3)_2]_2$.

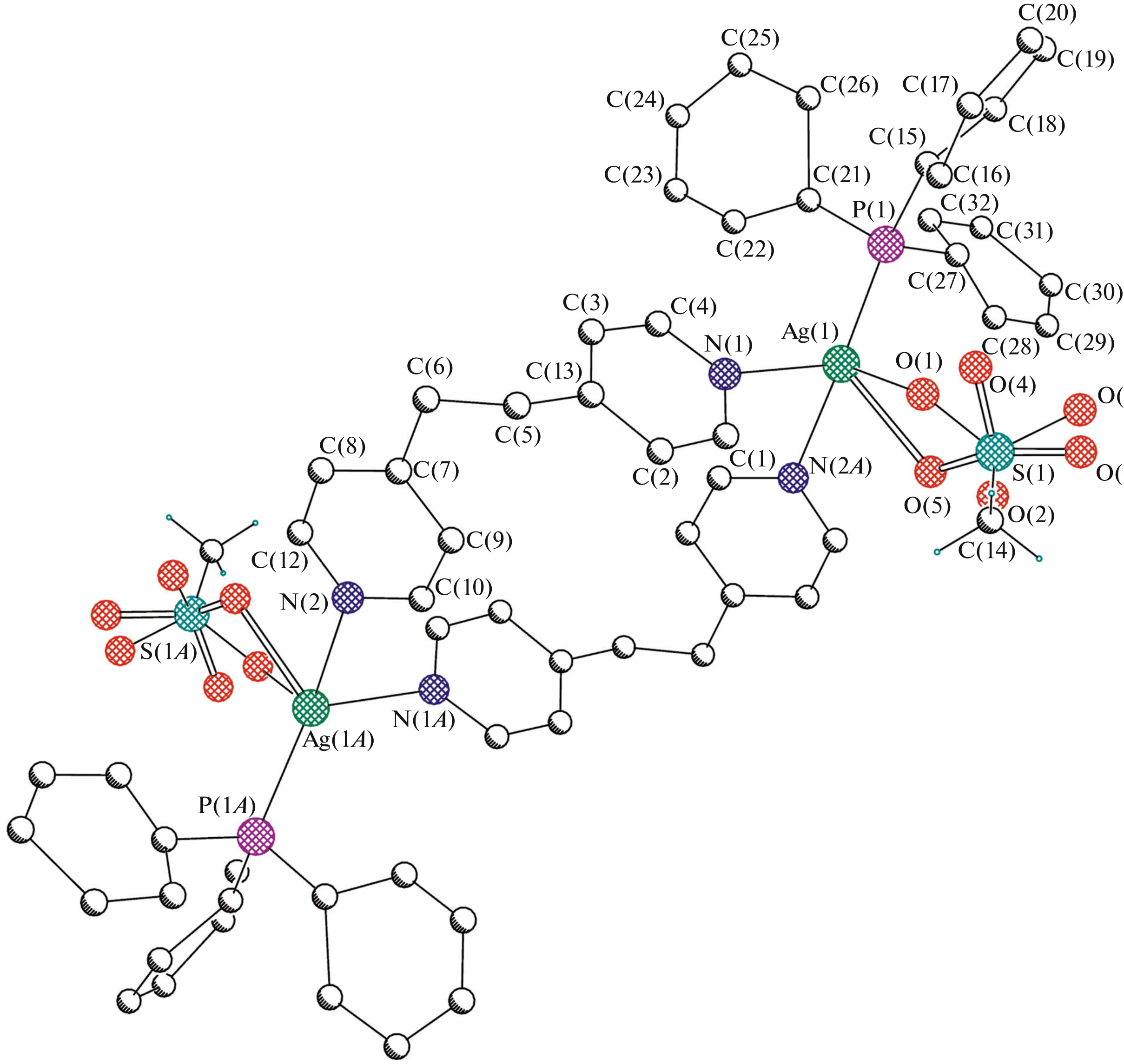

Fig. 2. Centrosymmetric binuclear structure [$Ag(CH_3SO_3)(PPh_3)(Dpe)$].

Phen, bis(2-pyridyl)amine, and so on) afford monomeric compounds like $[AgPPh_3L]^+X^-$ (L = chelating ligand) with the Ag : PPh_3 ratio of 1 : 1; only in the case of the CH_3COO^- anions, structures with bridging acetate groups are formed.

Figure 3 shows the PL spectra of compounds **I** and **II**. Both complexes tend to emit in blue and green spectral regions. Figure 4 shows the PL spectrum of free Dpe, which represents a superposition of two intense bonds centered at 467 and 546 nm (blue and green spectral regions, respectively).

As can be seen from the PL spectrum of the compound $Ag(PPh_3)_2(CH_3SO_3)$, the bands are in the range of 424–484 nm. Free PPh_3 shows luminescence at 500 [27] and 447 nm [28]. When PPh_3 is coordinated to d^{10}-metal ions, luminescence occurs at

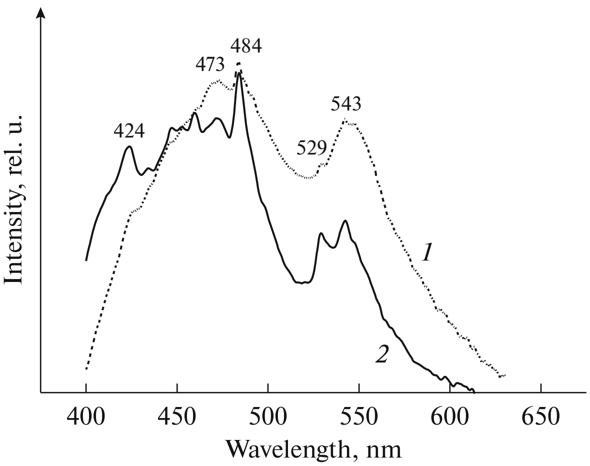

Fig. 3. Luminescence spectra of (*1*) [$Ag(CH_3SO_3)$-(PPh_3)(Dpe)] at λ_{exc} = 360 and (*2*) [$Ag(CH_3SO_3)$-$(PPh_3)_2]_2$ at λ_{exc}= 340 nm.

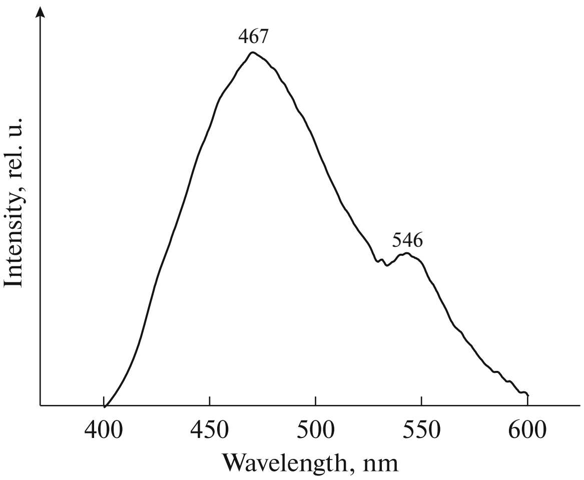

Fig. 4. Luminescence spectrum of free 1,2-dipyridylethane at λ_{exc}= 340 nm.

487 nm for $Ag(PPh_3)_2(L^1)$ (L^1 = *p*-toluenesulfonate) [27], at 481 nm for $Ag(PPh_3)_3BPh_4$, and at 513 nm for $Ag(PPh_3)_2Cl$ [27]. It has been noted [27] that luminescence is associated with the π^*–π-transitions of the PPh_3 phenyl ring. The luminescence spectrum of free Dpe exhibits two intense bands at 467 and 546 nm. The liminescence spectrum of the compound $[Ag_2(PPh_2Py)_2(CF_3COO)_2]$ in which the Ag^+ coordination sphere incorporates P and N atoms shows a band at 497 nm [29]. The data on the luminescence of free and coordinated PPh_3 together with the data of [29] attest that the spectrum of compound **II** is caused by the intraligand charge transfer.

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