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Dedicated to Academician Yu.A. Zolotov in the year of his 90th birthday

Halogen or Arene: Complexation of 4,4'-Dibromobiphenyl with a Trinuclear Silver(I) Macrocycle

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Abstract—A new complex of trinuclear silver(I) pyrazolate macrocycle $[AgPz]_3$ (Pz = $(CF_3)_2Pz$) with 4,4'-dibromobiphenyl (L) was synthesized and characterized. As shown by NMR spectroscopy, X-ray diffraction (CCDC no. 2169289), and quantum chemical calculations, the π-electron density of the aromatic ligand serves as the coordination site both in solution and in the solid state. The bromine atom is not coordinated to the metal. The complexation gives rise to infinite columns composed of alternating macrocycle and biphenyl molecules $\{[AgPz]_3 \cdot L\}_\infty$. The neighboring columns are linked by shortened Br–F^{CF3} contacts. In the solid state, the biphenyl geometry is flattened (the dihedral angles are 0.68° and 0.51°), which has the crucial effect on the photophysical behavior of the complex and demonstrates the possibility of controlling photoluminescence properties of oligophenylene systems.

Keywords: 4,4'-dibromobiphenyl, trinuclear silver(I) pyrazolate, complexation, X-ray diffraction, photoluminescence

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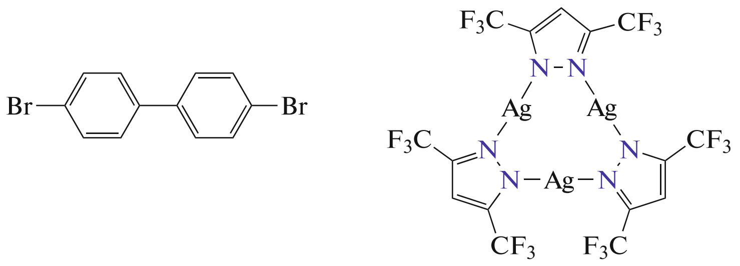
INTRODUCTION

Trinuclear complexes of Group 11 metals formed by Au(I)/Ag(I)/Cu(I) cations and anionic pyrazolate bridging ligands represent an extensive class of compounds [1]. The main core is the nine-membered metal–nitrogen M3N6 ring. The planar structure of the macrocycle gives rise to metallophilic interactions in the solid state, inducing their photophysical behavior via the formation of exciplexes [2–4]. Trinuclear copper(I) and silver(I) pyrazolates are Lewis acids, which opens up the possibility of complex formation via noncovalent binding to a broad range of bases [5–7]. As an example, consider the interaction with the π-electron systems of aromatic compounds and alkynes [8], hydride and halide ligands [9–13], and carbonyl compounds [14, 15]. Weak noncovalent interactions affect the emission spectra of both the initial macrocycle and the coordinated base. Meanwhile, strong coordination interactions with phosphorus- or nitrogen-containing ligands induce rearrangement of the trinuclear macrocycle and give rise to new emission characteristics [16–19].

As a continuation of our research of the complex formation between cyclic macrocycles of d^{10} metals and bases, here we studied the interaction of trinuclear silver(I) 3,5-bis(trifluoromethyl)pyrazolate ($[AgPz]_3$) with 4,4'-dibromobiphenyl (L) (Scheme 1). This compound possesses two potential sites of coordination to the macrocycle: π-electron density and the halogen atom. On the other hand, ligand L exhibits bright fluorescence, which depends on the physical state. The presence of a heavy atom (bromine) provides the possibility of phosphorescence due to coordination to Lewis–Brønsted acids [20]. As a result, the coordination sites in the solution and in the solid phase were identified, and the complex was isolated in a pure state and characterized by X-ray diffraction. The photoluminescence of the obtained complex in the solid state was studied and the relationship with the observed intermolecular interactions was established.



4,4'-Dibromobiphenyl, L

Macrocycle, $[AgPz]_3$

Scheme 1.

EXPERIMENTAL

All reactions were carried out in an argon atmosphere using the Schlenk technique. Solvents were purified by distillation under argon immediately prior to use. The initial $[AgPz]_3$ macrocycle was synthesized by a reported procedure [21]. 4,4'-Dibromobiphenyl (Sigma-Aldrich) was used as received. Analysis for carbon, nitrogen, and hydrogen was carried out on a Carlo Erba Model 1106 analyzer.

Synthesis of $\{[Br(C_6H_4)(C_6H_4)Br][(Ag[3,5-(CF_3)_2Pz])_3]\}$ (I). The macrocycle $[Ag(3,5-(CF_3)_2Pz)]_3$ (10 mg, 0.0107 mmol) was added to a solution of 4,4'-dibromobiphenyl (3.3 mg, 0.0107 mmol) in a hexane–CH_2Cl_2 mixture (v/v = 1 : 1, 2 mL). Slow evaporation of the solvent at 25°C resulted in the precipitation of colorless crystals, which were separated by decantation. The yield of the crystalline phase was 5.7 mg (43%).

For $C_{27}H_{11}N_6F_{18}Br_2Ag_3$

Anal. calcd., %	C, 26.05	H, 0.89	N, 6.75
Found, %	C, 26.18	H, 0.95	N, 6.72

Single crystal X-ray diffraction study of complex **I** was carried out on a Bruker APEX-II CCD diffractometer (MoK_α radiation, graphite monochromator, ω-scan mode). The structure was solved using the ShelXT program package [22] and refined by full-matrix least squares on F^2_{hkl} with anisotropic thermal parameters for all non-hydrogen atoms using the ShelXL program [23] included in the Olex2 package [24]. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement in the riding model. Selected crystallographic data for structure **I** are summarized in Table 1.

The structural data were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2169289; http://www.ccdc.cam.ac.uk).

^1H and ^{13}C NMR spectra were measured in a CCl_4/CD_2Cl_2 mixture (v/v = 9 : 1) on a Varian Inova 400 spectrometer operating at 400 MHz for protons. The chemical shifts (δ, ppm) were referred to the residual solvent signals (5.32 ppm for ^1H and 54 ppm for ^{13}C in CD_2Cl_2). Photoluminescence spectra were recorded on a Shimadzu RF-6000 spectrofluorimeter. The powdered samples were placed in quartz capillaries.

RESULTS AND DISCUSSION

To begin the study of complex **I**, we investigated the complexation in solution by NMR spectroscopy. Most information is provided by ^{13}C NMR spectra as the carbon signals of the base are highly sensitive to the complexation. The measurements were carried out in a 9 : 1 (v/v) mixture of nonpolar CCl_4 and CD_2Cl_2. We showed that the complexation of macrocycles with the bases should better be carried out in least polar media, because this promotes the shift of the equilibrium towards the reaction products owing to increase in the formation constants. For example, on going from low-polar CH_2Cl_2 to non-polar hexane, the complex formation constants increase by two orders of magnitude [5, 25]. The addition of one equivalent of the macrocycle to a solution of L induced both downfield and upfield shifts of the signals of diphenyl carbon atoms. These shifts are typically observed upon complexation of macrocycles with aromatic systems and attest to different involvement of carbon atoms into coordination to the metal atoms of the macrocycle. For example, upfield shifts are observed for the signals of carbon atoms that participate in the interaction, whereas the signals of atoms not involved in the interaction undergo downfield shifts. The observed changes are shown in Fig. 1.

Note that the symmetry of the biphenyl base does not fundamentally change upon complex formation and that the largest shifts are observed for the carbon atoms of the central part of the molecule. The positions of the carbon signals for free 4,4'-dibromobiphenyl and for 4,4'-dibromobiphenyl in the presence of the silver macrocycle are presented below.

Compound	Number of the carbon atom			
	1	2	3	4
Free L	138.89	128.44	131.99	121.98
L + $[AgPz]_3$	138.29	128.06	132.09	122.12

Table 1. Crystallographic data and X-ray experimental and structure refinement details for **I**

Parameter	Value
Molecular formula	$C_{27}H_{11}N_6F_{18}Br_2Ag_3$
M	1244.85
T, K	120
System	Triclinic
Space group	$P\bar{1}$
a, Å	12.34(3)
b, Å	12.73(4)
c, Å	12.96(4)
α, deg	81.45(7)
β, deg	65.45(5)
γ, deg	76.45(7)
V, Å^3	1797(9)
Z	2
ρ(calcd.), g cm^{-3}	2.301
μ, mm^{-1}	3.968
F(000)	1176
2θ range for the whole set of data, deg	3.94 to 51.994
Number of measured reflections	17380
Number of unique reflections (R_{int})	7015 (0.0317), $R_{sigma} = 0.0394$
Data/constraints/parameters	7015/0/505
GOOF	1.024
R-factors ($I > 2\sigma(I)$)	$R_1 = 0.0429$, $wR_2 = 0.1255$
R-factors (for all reflections)	$R_1 = 0.0498$, $wR_2 = 0.1330$
Residual electron density (max/min), e Å^{-3}	2.15/–1.62

The ^{1}H NMR spectrum also shows an upfield shift of all proton signals of L ($\Delta\delta = -0.1$ ppm) in the presence of one equivalent of $[AgPz]_3$ (Fig. 2).

Complex **I** was isolated in the solid state and characterized by X-ray diffraction analysis. In the crystal, the complex occurs in a general position and contains one macrocycle molecule per base molecule (Fig. 3). In ligand L, a crystallographic symmetry center is located in the middle of the bond between the aromatic substituents; this results in equivalence of substituted phenyl moieties. The coordination to silver involves only the π-electron density of aromatic substituents. The lengths of the Ag...C contacts are in the range of 3.164–3.414 Å, thus demonstrating the formation of relatively strong bonds [26]. In the crystal, the macrocycle and L molecules alternate to form an infinite column. The alternating 4,4'-dibromobiphenyl molecules are arranged perpendicularly, while the macrocycle molecules are packed in the head-to-tail pattern.

Actually, the crystal packing is composed of alternating two macrocyclic silver(I) pyrazolates and two 4,4'-dibromobiphenyls in which the dihedral angles and bond lengths somewhat differ. Indeed, in one L molecule, the coordination to the macrocycle induces elongation of the bond between the benzene rings up to 1.510(1) Å versus 1.486(6) Å in another L molecule and versus 1.48 Å in free biphenyl [20, 27]. In the complex, the 4,4'-dibromobiphenyl has a planar geometry (the dihedral angles are 0.68° and 0.51°), whereas in the free molecule, the rings are markedly rotated (by approximately 40°).

In the complex, the plane of the macrocycle is substantially distorted, which is caused by coordination to two base molecules located on both sides of $[AgPz]_3$ at an angle of 90° relative to each other.

Also, the crystal packing has shortened Br...F contacts (3.254(7) Å), which bind neighboring stacks to give 2D layers (Fig. 4).

The noncovalent interactions in the crystal of **I** were studied by the NCI method [28, 29] (Fig. 5). It can be seen that stronger interactions (blue areas of isosurface) are observed between the carbon and silver

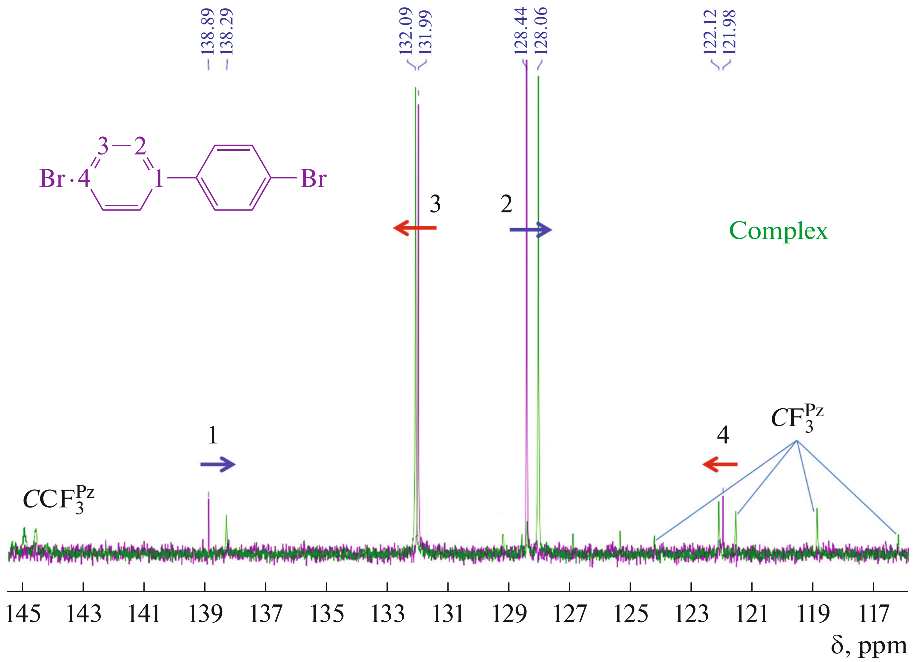


Fig. 1. ^{13}C NMR spectrum of the starting 4,4'-dibromobiphenyl in a CCl_4–CD_2Cl_2 mixture (9 : 1; violet) and in the presence of one equivalent of $[AgPz]_3$ (green). The blue arrow indicates an upfield shift and the red arrow shows a downfield shift.

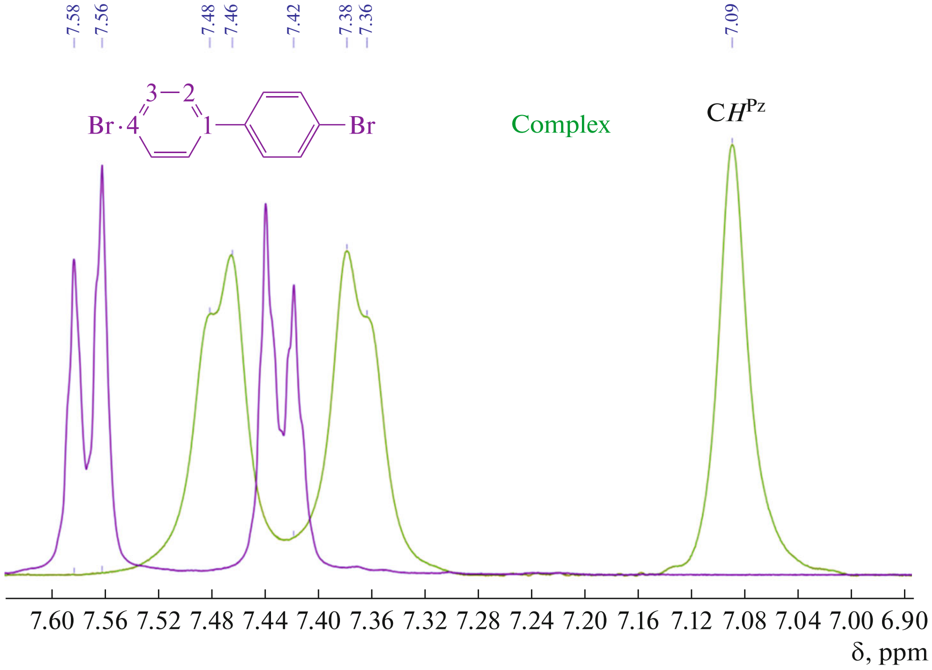


Fig. 2. ^{1}H NMR spectrum of initial 4,4'-dibromobiphenyl in a CCl_4–CD_2Cl_2 mixture (9 : 1; violet) and in the presence of one equivalent of $[AgPz]_3$ (green).

atoms, which confirms the assignments based on NMR spectroscopy and X-ray diffraction.

The photoluminescence of complex **I** in the solid state was studied. The luminescence spectrum of free 4,4'-dibromobiphenyl shows a structured band with a maximum at 415 nm, typical of ligand-centered fluorescence (^{1}LC, Fig. 6) [20]. The formation of the complex leads to a significant shift of the emission band to

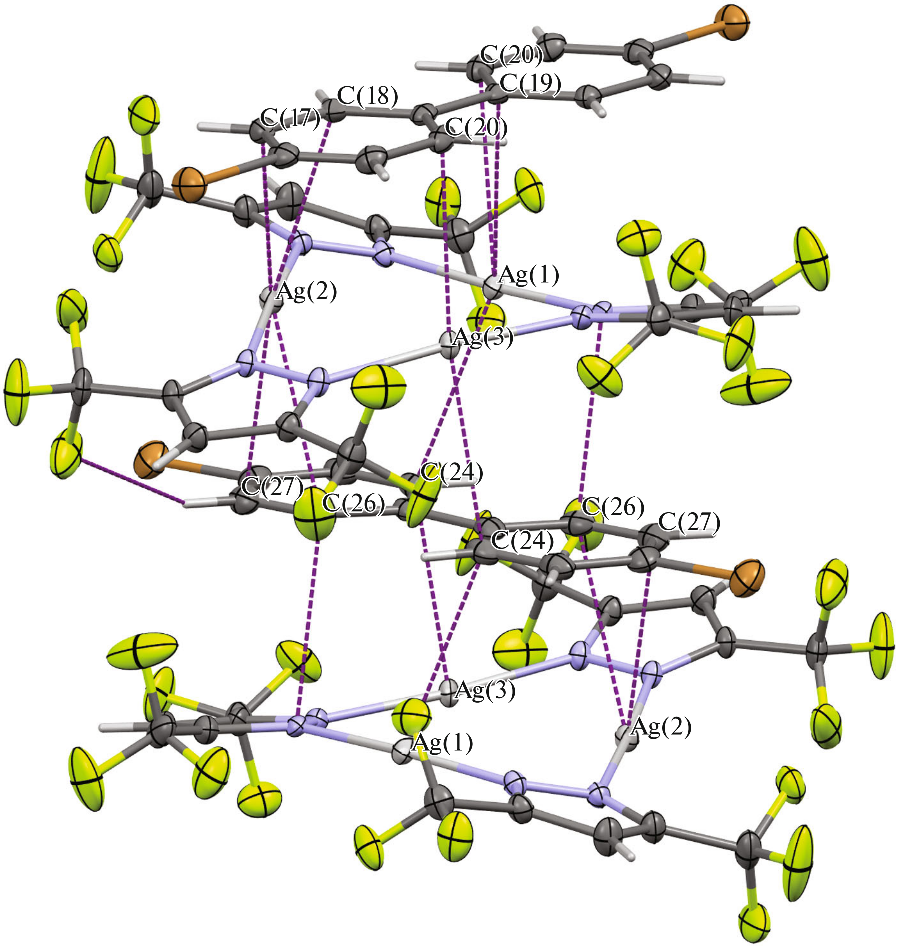


Fig. 3. Fragment of the crystal packing for complex **I** illustrating the formation of an infinite column via alternation of molecules of the complex.

lower energy (the maximum at 505 nm, Fig. 6). The band is broadened, with its structure being retained, which attests to the same nature of the emission (centered on the ligand). The formation of the complex results in a considerable change in the excitation spectrum and shift of the maximum to higher energy (to 310 nm). The position of the emission band indicates that the complex formation is accompanied by phosphorescence. Evidently, this is caused by the planar geometry of 4,4'-dibromobiphenyl in complex **I** and by the heavy atom (silver) effect.

In conclusion, it is noteworthy that the reaction of trinuclear silver(I) 3,5-bis(trifluoromethyl)pyrazolate with 4,4'-dibromobiphenyl affords a complex in solu-

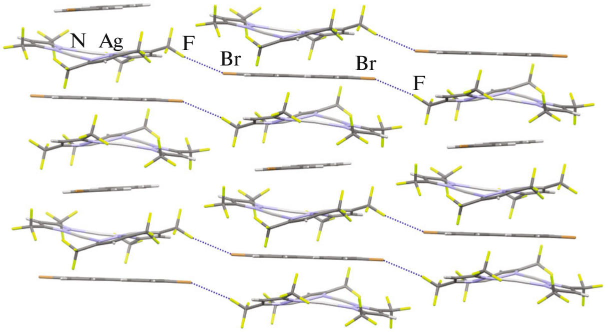


Fig. 4. Fragment of the crystal packing for complex **I** illustrating the formation of 2D layers via shortened Br...F contacts.

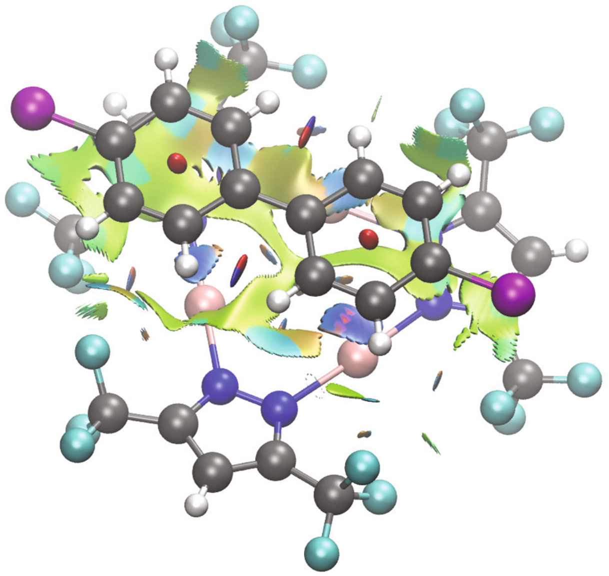


Fig. 5. NCI surface (0.25 a.u. isosurface in the scale BGR −1.5(B)...0(G)...+1.5(R)) showing the stabilizing interaction (blue) and regions of van der Waals interactions (green).

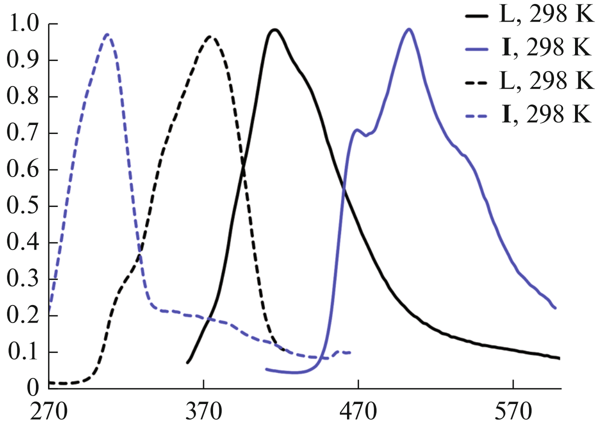


Fig. 6. Normalized emission (continuous line) and excitation (dashed line) of free L (black) and complex **I** (blue) at 298 K.

tion and in the solid state. In solution, NMR study showed the existence of weak interactions between the macrocycle and carbon atoms in the low-polar medium. The upfield shift of ^{13}C signals attests to different types of participation of base moieties in the coordination to the macrocycle. In the solid state, 1 : 1 complexes are formed (i.e., one base molecule per macrocycle molecule), being connected into infinite columns. A change in the geometry of the biphenyl moiety to fully planar gives rise to bright phosphorescence of the complex.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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