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Dinuclear Silver(I) Nitrate Complexes with Bridging Bisphosphinomethanes: Argentophilicity and Luminescence

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Abstract: Two silver nitrate complexes with bisphosphines were obtained and characterized: $[Ag(dcypm)]_2(NO_3)_2$ (1; dcypm = bis(dicyclohexylphosphino)methane) and $[Ag(dppm)]_2(Me_2Pz^H)_n$ $(NO_3)_2$ (n = 1, 2a; n = 2, 2b; dppm = bis(diphenylphosphino)methane, Me₂Pz^H = 3,5-dimethylpyrazole). The steric repulsions of bulky cyclohexyl substituents prevent additional ligand coordination to the silver atoms in 1. Compounds obtained feature the bimetallic eight-member cyclic core [AgPCP]₂. The intramolecular argenthophilic interaction (d(Ag - Ag) = 2.981 Å) was observed in complex 1. In contrast, the coordination of pyrazole led to the elongation of Ag. Ag distance to 3.218(1) Å in 2a and 3.520 Å in 2b. Complexes 1 and 2a possess phosphorescence both in the solution and solid state. Time-dependent density-functional theory (TD-DFT) calculations demonstrate the origin of their different emission profile. In the case of 1, upon excitation, the electron leaves the Ag-P bonding orbital and locates on the intramolecular Ag...Ag bond (metal-centered character). Complex **2a** at room temperature exhibits a phosphorescence originating from the ${}^{3}(M + L^{P+N})L^{Ph}CT$ state. At 77 K, the photoluminescence spectrum of complex 2a shows two bands of two different characters: ${}^{3}(M + L^{P+N})L^{Ph}CT$ and ${}^{3}LC^{Ph}$ transitions. The contribution of Ag atoms to the excited state in both complexes 2a and 2b decreased relative to 1 in agreement with the structural changes caused by pyrazole coordination.

Keywords: silver phosphine; pyrazole; luminescence; TD-DFT

1. Introduction

The non-covalent metal–metal interactions play a significant role in the emission [1,2] or catalytic [3–5] properties of the d¹⁰ metal complexes. Dinuclear or trinuclear coinage metal complexes with bridging bis- or trisphosphine ligands represent a unique class of molecules occupying a position between mononuclear complexes and nanoparticles. They have remarkable chemical and physicochemical properties due to the presence of metal–metal bonds of various energy [6]. For example, di- and tetranuclear silver nitrates with bis(diphenylphosphino)methane are known since 1983 [7]. The metal-centered (MC) nature of emission is well known for coinage metal complexes with bridging phosphines. Already in 1989, Che et al. showed on an example of gold dimer $[Au_2(dppm)_2]^{2+}$

that shortened Au–Au distances participate in electron transitions [8]. Then, on the example of silver dinuclear complexes with bisphosphines $[Ag(dcypm)]_2X_2$ (X = PF₆⁻, and CF₃SO₃⁻, or CN⁻; dcypm = bis(dicyclohexylphosphino)methane) [9,10] and $[Ag(dmb)]_2X_2$ complexes (X = Cl, Br, I; dmb = 1,8-diisocyano- ρ -menthane) [11], it has been shown that UV–Vis (Ultraviolet–visible) absorption band of complexes to d–p transition from intramolecular argentophilic interaction. The metallophilic nature of this band corresponding to the stretching Ag–Ag vibration (80 cm⁻¹) was proven by Raman spectroscopy with excitation at the UV maximum [9]. The same behavior has also been observed for metallothioneins [11,12] and nanoclusters [13,14]. The interaction between two coinage metal ions has been investigated by spectral as well as computational methods [15,16]. Recently, using the example of Au/Ag di- and trinuclear complexes with diphosphanyl NHC ligands, this phenomenon was explained experimentally and theoretically [17].

Surprisingly, despite the wide structural diversity of coinage metals and bisphosphine complexes, there is practically no information about silver(I) nitrate complexes. Herein, we present the synthesis, structures, photophysical properties of dinuclear silver(I) bisphosphines $[Ag(dcypm)]_2(NO_3)_2$ (1) (dcypm = bis(dicyclohexylphosphino)methane) and $[Ag(dppm)]_2(Me_2Pz^H)_n(NO_3)_2$ (n = 1, **2a**; n = 2, **2b**) (dppm = diphenylphosphino)methane) with 3,5-dimethylpyrazole (Scheme 1). The influence of Ag...Ag distances or the ligand at silver atoms on the emission properties will be discussed involving the theoretical interpretation.



R=Ph or Cy

Scheme 1. Representation of central [MPCP]₂ core for the complexes studied (R = Cy(1), Ph (2)).

2. Materials and Methods

¹H and ³¹P{¹H} nuclear magnetic resonance (NMR) measurements were carried out on a Bruker Avance 400 spectrometer. Infrared (IR) spectra were collected on a Shimadzu IR Prestige-21 FT-IR (Fourier-transform infrared spectroscopy) spectrometer using KBr pellets. The photoluminescence spectra and lifetime measurements of the phosphors were recorded at 77 K and 298 K on a Fluorolog-3 spectrofluorometer system (HORIBA Jobin-Yvon, the excitation source was a 450 W xenon lamp with Czerny–Turner double monochromators, and the registration channels were a R928 photomultiplier, while a 150 W pulsed xenon lamp was used for lifetime measurements). The powders for these measurements were packed in quartz capillaries. The phosphorescence quenching curves were analyzed using the FluoroEssence[™] software for calculation of the phosphorescence lifetime values. The UV–Vis spectra were measured on a Cary50 spectrometer.

X-ray diffraction study. Single-crystal X-ray diffraction experiments for complexes 1, 2a, and 2a/2b were carried out with a Bruker SMART APEX II diffractometer. The structures were solved by the direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of methyl, methylene, and aromatic fragments were calculated according to those idealized geometries and refined with constraints applied to C–H and N–H bond lengths and equivalent displacement parameters ($U_{eq}(H) = 1.2U_{eq}(X)$, where X is the central atom of the XH₂ group; and $U_{eq}(H) = 1.5U_{eq}(Y)$, Y—central atom of YH₃ group). All structures were solved with the ShelXT program [18] and refined with the ShelXL program [19]. Molecular graphics were drawn using the OLEX2 program [20]. The cyclohexyl fragment in complex 1, Me₂Pz^H ligand in complex 2a, and in the second molecule

in co-crystal **2a/2b** were disordered, and the occupancy of positions of disordered levels was 0.5. Nitrate anions in the second molecule (**2a**) in co-crystal **2a/2b** were disordered, and the occupancy of positions of disordered levels were 0.3 and 0.7. CCDC 2013947, 2013948, and 2033764 contained the supplementary crystallographic data for complexes **1**, **2a**, and **2a/2b**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures. Crystal data and structure refinement parameters are presented in Table 1.

	1	1 2a		
Empirical Formula Formula weight	C ₂₅ H ₄₆ AgNO ₃ P ₂ 578.44	$\begin{array}{c} C_{55}H_{53}Ag_2N_4O_6P_4\\ 1205.63\end{array}$	$C_{117}H_{116}Ag_4Cl_2N_5O_6P_4$ 2675.24	
	Bruker SMART APEX	Bruker SMART APEX	Bruker SMART APEX	
Diffractometer	CCD	CCD	CCD	
Scan mode	ϕ and ω scans	ϕ and ω scans	ω and ϕ scans	
Anode [Wavelength, Å]	MoK α [0.71073] sealed MoK α [0.71073] sealed		MoKα [0.71073] sealed	
	tube tube		tube	
Crystal Dimensions, mm	$0.1\times0.15\times0.36$	$0.08\times0.11\times0.15$	$0.08\times0.12\times0.44$	
Crystal color	colorless	colorless	colorless	
Crystal system	tetragonal	monoclinic	triclinic	
a, Å	29.8637(11)	10.940(2)	10.9934(13)	
b, Å	29.8637(11)	19.805(4)	11.9540(14)	
c, Å	12.6441(5)	11.719(2)	22.858(3)	
α, deg	90	90	77.727(2)	
β, deg	90	91.087(4)	82.796(2)	
γ, deg	90	90	85.688(2)	
Volume, Å ³	11276.5(9)	2538.5(9)	2908.5(6)	
Density, $g \text{ cm}^{-3}$	1.363	1.577	1.527	
Temperature, K	120	120	120	
Tmin/Tmax	0.7056/0.7461	0.6339/0.7460	0.6141/0.7459	
μ , mm ⁻¹	0.853	0.953	0.930	
Space group	I4 ₁ /a	$P2_1/n$	P1	
Ž	16	2	2	
F(000)	4864	1226	1360	
Reflections collected	54587	23611	37353	
Independent reflections	5546	4995	16342	
Reflections (I > 2σ (I))	4576	3545	9421	
Parameters	234	308	740	
R _{int}	0.0350	0.1053	0.0860	
20min–20max	2.728-51.998	4.040-52.000	3.670-59.410	
wR_2 (all reflections)	0.2032	0.1571	0.1221	
$R_1 (I > \sigma (I))$	0.0717	0.0866	0.0866 0.0561	
GOF	1.027	1.220	0.972	
$ ho_{min}/ ho_{max}$, $e Å^{-3}$	-1.042/1.733	-1.338/0.927	-1.011/1.385	

Table 1. Crystallographic data for complexes 1, 2a, and 2a/2b.

Computational details. Full geometry optimizations of complexes **1** and **2** were performed using the PBE0 functional [21] and SVP (split valence polarization) basis set [22,23] without any symmetry restrictions using Gaussian09 software [24]. Optimized geometries of **1**, **2a**, and **2b** reasonably reproduced the X-ray geometry (Figure S14 in the Supplementary Materials). The equilibrium geometry for **1** and **2b** had a C_i symmetry point group (as it was found by X-ray analysis), leading to the symmetry forbidden electronic transitions, so only transitions of A_u symmetry were analyzed. For complex **2a**, the second pyrazole molecule was left, but rotated to be in the Me₂PzH ligand position of a neighbor complex in the crystal. Herewith, that molecule remained non-bonded by the Ag–N bond, but its presence helps to keep the complex similar to the X-ray characterized one. Vertical singlet and triplet excitations were calculated by TD-DFT on the same level of theory. Analysis of the excited

states was done with the Multiwfn program [25]. The similarity of the excited states was analyzed by the approach suggested by Chen [26].

$$s_{H/E} = 1 - \frac{\sum_i \left| a_i - b_i \right|}{2}$$

where a_i and b_i are contributions of the *i* atom to the hole (s_H) or electron (s_E) in the states *a* and *b*.

Synthesis. All operations were performed with Schlenk techniques under a dry argon atmosphere. Commercially available solvents and ligands were used without additional purification.

[**Ag(dcypm)**]₂(**NO**₃)₂ (1). Mixture of AgNO₃ (50 mg, 0.294 mmol) and bis(dicyclohexylphosphino) methane (120 mg, 0.294 mmol) was stirred in 5 mL of CH₂Cl₂ at room temperature for 3 h. A white solid was afforded upon precipitation by n-hexane. The precipitate formed was filtered, washed with 10 mL of acetone, and dried in vacuum. Yield 91%. NMR (CD₂Cl₂, ppm) ¹H: δ = 1.19–2.13 ppm (m, 88 H^{Cy} and 4 CH₂), ³¹P{¹H}: δ = 28.8 (m, 4P). Anal. calcd/found for C₅₀H₉₂Ag₂N₂O₆P₄: C, 51.91/52.01; H, 8.02/8.08; N, 2.42/2.40.

[Ag(dppm)]₂(Me₂Pz^H)(NO₃)₂ (2a). The suspension of 50 mg of AgNO₃ (0.294 mmol) and 17.3 mg of 3,5-dimethylpyrazole (0.180 mmol) was stirred in 10 mL of acetone for the one hour until a slurry precipitate was formed, and then the solution of dppm (113 mg, 0.294 mmol) in 3 mL of acetone was added. The reaction mixture was stirred overnight at room temperature. The precipitate formed was filtered off and washed with 10 mL of CH₂Cl₂. The solution obtained was added to 20 mL of hexane, and the mixture was kept in the refrigerator at ca. 5 °C for one hour. The precipitate formed was filtered off, washed with hexane, and both solids were combined and dried under reduced pressure. Complex **2a** was obtained by slow crystallization at room temperature from boiling CH₃CN solution of small portions of these solids. Yield 68%. NMR (CD₃CN, ppm) ¹H: δ = 2.07 ppm (s, 6H, Me^{Pz}), 3.71 ppm (m, 4H, CH₂^{dppm}), 5.74 ppm (s, 1H, CH^{Pz}), 7.20–7.44 (m, 40H, Ph^{dppm}), ³¹P{¹H}: δ = 7.5 (m, 4P); IR (KBr, cm⁻¹): v 3201 (vNH), 3138, 3050, 2922, 2876 (vCH), 1580. Anal. calcd/found for C₅₅H₅₄Ag₂N₄O₆P₄: C, 54.75/54.07; H, 4.51/4.24; N, 4.64/4.60.

3. Results and Discussion

3.1. Synthetic Procedures

Complex 1 was obtained by the interaction of AgNO₃ with bis(dicyclohexylphosphino)methane (dcypm) in dichloromethane (DCM) and subsequent precipitation with hexane. Moreover, the addition of dcypm to the solution of the complex [Ag(Me₂Pz^H)]NO₃ generated in situ only led to complex **1** with high yield. This suggests that the steric effect of bulk cyclohexyl substituents makes impossible the pyrazole coordination to the silver atoms. In contrast, mixing AgNO₃ with 3,5-dimethylpyrazole and less sterically demanding bis(diphenylphosphino)methane (dppm) in acetone led to the formation of the precipitate. The elemental analysis and ¹H NMR spectrum demonstrated that the composition of the bulk solids corresponded to the complex [Ag₂(Me₂PzH)(dppm)]₂(NO₃)₂ (**2b**) containing two pyrazole molecules per [Ag(dppm)]₂(NO₃)₂ moiety (Figures S19 and S20). Unfortunately, reprecipitation or crystallization of this complex at low temperatures led to the partial loss of pyrazole molecules, resulting in a mixture of complexes [Ag(dppm)]₂(Me₂Pz^H)(NO₃)₂ (**2a**) [Ag₂(Me₂Pz^H)(dppm)]₂(NO₃)₂ (**2b**). In a pure form, only complex **2a** could be obtained by slow crystallization from boiling acetonitrile solution at room temperature. It should be noted that the elimination of the second 3,5-dimethylpyrazole molecule was not observed.

3.2. Crystal Structure of Complexes

The structures of compounds obtained were proved by single-crystal X-ray diffraction. The crystallographic data and structure refinement details are summarized in Table 1, and the relevant bond distances and angles are collected in Table 2.

Bonds Lengths			Angles				
1		2		1		2	
Ag1-P1	2.396(2)	Ag1-P1	2.403(2)	Ag1-Ag1-P2	82.90(4)	Ag1-Ag1-P2	81.59(5)
Ag1-O1	2.557(9)	Ag1-O1	2.554(6)	Ag1-P1-C1	111.1(2)	Ag1-01-N3	129.8(5)
Ag1-Ag1	2.9810(7)	Ag1-N1	2.443(6)	Ag1-P1-C2	115.5(2)	Ag1-N1-N2	124.7(5)
Ag1-P2	2.428(2)	Ag1-Ag1	3.218(1)	Ag1-P1-C8	113.2(3)	P1-Ag1-O1	126.5(1)
P1-C1	1.838(8)	Ag1-P2	2.442(2)	Ag1-01-N1	106.9(5)	P1-Ag1-N1	98.6(2)
P1-C2	1.850(6)	P1-C4	1.846(8)	P1-Ag1-O1	119.1(2)	P1-Ag1-Ag1	88.90(5)
P1-C8	1.85(1)	P1-C17	1.801(8)	P1-Ag1-Ag1	94.21(4)	P1-Ag1-P2	151.61(8)
P2-C1	1.827(7)	P1-C23	1.828(8)	P1-C1-P2	114.4(3)	O1-Ag1-N1	84.1(2)
P2-C17	1.84(1)	P2-C4	1.822(8)	P1-Ag1-P2	152.22(6)	O1-Ag1-Ag1	91.5(1)
P2-C23	1.844(6)	P2-C5	1.827(8)	O1-Ag1-Ag1	74.4(2)	O1-Ag1-P2	80.7(1)
O1-N1	1.27(1)	P2-C11	1.804(8)	O1-Ag1-P2	86.9(2)	N1-Ag1-Ag1	172.5(2)
O2-N1	1.244(8)	P2-Ag1	2.442(2)	Ū		N1-Ag1-P2	91.7(2)
O3-N1	1.12 (1)	O1-N3	1.25(1)			N2-N1-C1	101.8(6)
		O2-N3	1.24(1)				
		O3-N3	1.24(1)				
		N1-N2	1.31(1)				
		N1-C1	1.50(1)				
		N1-C2	1.58(1)				
		N2-C3	1.34(1)				
		N2-C2	1.02(1)				

Table 2. Selected geometric parameters (bond lengths in Å, angles in degrees) for complexes 1 and 2a.

Colorless crystals of complex **1** was obtained by slow evaporation of their DCM/hexane (v/v = 2:1) solutions at ca. 5 °C. Complex **1** features a chair form of the eight-member cyclic [AgPCP]₂ core (Figure 1), in which silver atom is coordinated to four atoms (two P^{dppm} (2.396(2) and 2.429(2) Å), O^{Nitrate} (2.558(9) Å) and Ag (2.9812(7) Å), forming the distorted triangular pyramidal or tetrahedron environment (Figure 2). The angles ∠P1-Ag1-P2, ∠P1-Ag1-O1, ∠P1-Ag1-Ag1, ∠O1-Ag1-Ag1 were 152.22(6)°, 119.1(2)°, 94.21(4)°, and 74.4(2)°, respectively. There were only several examples of the similar [Ag(dcypm)]₂²⁺ core with PF₆⁻, CF₃SO₃⁻ [9], and CN⁻ [10] counter ions. Observed Ag–Ag bond length (2.9812(7) Å) was in the range of shared argentophilic interactions [27–29] being non-significantly longer than that present in the literature (av. 2.93 Å). The central core [MPCP]₂ was similar for dinuclear silver bisphosphines, but additional κ^1 coordination of the nitrate anion led to a significant distortion of the central cycle. Silver atoms as well as CH₂ fragments lie out the P₄ plane for 0.557 and 0.607 Å, respectively. For example, the same parameters for complex with CN⁻ were 0.415 and 0.575 Å [10]. These structural peculiarities reflect the influence of the nitrate anion on the electronic properties of complexes (*vide infra*). The Ag–P bond lengths (2.396(2) and 2.429(2) Å) were typical for the silver bis-phosphines.

Supramolecular packing of 1 was realized via the network of weak C^{Cy}-H…O^{Nitrate} interactions of neighboring molecules (2.316 Å, \angle O-H-C = 156.1°; Figure 2) [30,31].

In contrast, in the case of interaction of the silver nitrate with dppm ligand and 3,5-dimethylpyrazole, complexes of different compositions were observed. As demonstrated above, the interaction led to the formation of the precipitate. Analysis of this solid indicates that it mainly contained one Ag atom per one dppm ligand and one Me₂Pz^H molecule. However, varying the crystallization conditions allowed for two different types of complexes. The solubility of the solids obtained was very low, and crystallization was performed from significantly diluted solutions (mM concentrations). The most stable one was complex **2a** containing one pyrazole molecule, crystals that could be obtained at different temperatures (-10, 0, or 25 °C) and from different solvents (MeOH, CH₃CN, and DCM/hexane mixture). Slow crystallization from the boiling CH₃CN at room temperature was the best condition for obtaining pure complex **2a**. Complex **2b** was obtained only as a co-crystal with **2a**, representing two independent molecules with one and two Me₂Pz^H molecules. This sample was crystallized

in an NMR tube after a ¹H NMR experiment in CD_2Cl_2 , which eventually showed the 1/1 ratio of $Me_2Pz^H/dppm$ in solution. These data demonstrate that crystallization from a diluted solution led to the elimination of one pyrazole from the complex $[Ag(dppm)Me_2Pz^H]_2(NO_3)_2$ (**2b**), resulting in a more stable $[Ag(dppm)]_2(Me_2Pz^H)(NO_3)_2$ (**2a**) complex.



Figure 1. X-ray diffraction (XRD) structure of complex 1 (carbon and hydrogen atoms are shown as sticks).



Figure 2. Supramolecular packing of 1.

Complex **2a** crystallizes in a chair form of the central [AgPCP]₂ cycle (Figure 3). There was only one molecule of pyrazole coordinated with one of the silver atoms in the crystal. The complex in the crystal was in the superposition of two possible isomers in which the pyrazole ligand coordinates by nitrogen to both silver atoms (occupation 0.5). This behavior leads to the presence of a pseudo inversion center at the center of the Ag–Ag distance. Interaction with Me₂Pz^H ligand led to the pentacoordinate environment distorted trigonal bipyramidal of one silver atom (two P^{dppm} (2.403(2) and 2.442(2) Å), N^{Pz} (2.446(6) Å), O^{Nitrate} (2.554(6) Å), and Ag (3.218(1) Å) (Figure 3). The angles P1-Ag1-P2, P1-Ag1-O1, and P1-Ag1-N1 were 151.61(8)°, 126.5(1)°, and 98.6(2)°, respectively. The presence of the 3,5-dimethylpyrazole ligand led to the κ^1 coordination of the nitrate to silver atoms in contrast to the

known $[Ag(dppm)]_2(NO_3)_2$ complex [7,32], which possesses the κ^2 coordination mode of the nitrate anion. Moreover, the coordination of pyrazole led to the elongation of the Ag–Ag distance to 3.218 Å, which was significantly longer than that for $[Ag(dppm)]_2(NO_3)_2$ (3.090–3.110 Å) [7,32]. The Ag–Ag distance was in the range of closed-shell metallophilic interactions [27]. Silver atoms as well as CH₂ fragments, were located on both sides of the P₄ plane lying out at 0.594 and 0.720 Å, respectively, which determines the chair-configuration of the central M₂P₄ core. It should be noted that Tiekink [32] also reported the same configuration for $[Ag(dppm)(NO_3)]_2$ with a more distorted central core in contrast to the boat form obtained by Bau [7]. The Ag–P bonds lengths in **2** (2.403(2) and 2.442(2) Å) are typical for the silver bis-phosphines complexes. The Ag–N^{Pz} bond length (2.446(4) Å) is typical for the silver phosphine complexes with donor aromatic nitrogen ligands [33,34]. The complex was stabilized via $O_1^{Nitrate}$...H–N^{Pz} intramolecular hydrogen bond (1.702 Å, $\angle O$ -H-N = 165.9°) [30,31].



Figure 3. XRD structure of the complex 2 (carbon and hydrogen atoms are shown as sticks).

Complex **2b** was obtained only in the form of a co-crystal of two molecules of general motif $[Ag(dppm)]_2(NO_3)_2$ with one and two pyrazoles, respectively (Figure 4). The part that contained one molecule of pyrazole was generally identical to compound **2a** with non-significant differences in bond lengths and angles. The second part was a dinuclear complex **2b** with two molecules of 3,5-dimethylpyrazole coordinated to both silver atoms. Complex **2b** also crystallized in a chair form of the central $[AgPCP]_2$ cycle. Moreover, there was the inversion center of this fragment in the middle of the Ag–Ag distance. The second pyrazole molecule's coordination led to the significant elongation of the Ag–Ag distance (3.520 Å). As a result, the presence of one or two coordinated ligands to the silver atoms in $[Ag(dppm)]_2$ cores led to the elongation of Ag–Ag distances and the absence of the shared intramolecular argenthophilic interactions. The Ag–P (2.446(1) and 2.422(1) Å) bond lengths were similar to those observed in complexes **1** and **2a**. The interaction of silver atoms with pyrazoles in **2b** was non-significantly stronger than that for **2a** in accordance with the correlation of the shortened Ag–N^{Pz} bond lengths (2.446(1) Å for **2a** and 2.381(4) Å for **2b**). In contrast, the coordination of addition pyrazole led to the significant elongation of the Ag–O^{Nitrate} bonds (2.554(6) Å for **2a** and 2.674 (3) Å for **2b**).



Figure 4. XRD structure of the co-crystal **2a/2b** and dichloromethane (DCM) molecule (carbon, hydrogen, and chlorine atoms are shown as sticks).

3.3. Photophysical Properties

The only pure compounds **1** and **2a**, in contrast to **2b**, were isolated. All experimental studies (UV–Vis and photoluminescence) were performed for these complexes. The theoretical investigations (TD-DFT) were performed for all possible types of complexes (**1**, **2a**, and **2b**).

The TD-DFT calculations were performed for complexes **1** and **2b** keeping their local C_i symmetry. The presence of the inversion center led to the appearance of the symmetry forbidden A_{g} , and the symmetry allowed Au transitions. This is why only symmetry allowed Au transitions are discussed further. The lowest excitations of 1 were S₁ and S₂ with energies of 4.18 and 5.01 eV (296 and 247 nm; Table S1), respectively. The S₁ had a pronounced LC^{NO3} character with a negligible impact of Ag atoms (Figure S1, Table S1). The oscillator strength (f) value of 0.0002 demonstrates that this excitation was ineffective (dark state). In contrast, the second singlet transition (5.01 eV, f = 0.1853) had a metal-centered (MC) nature (Figure 5). Upon this excitation, the electron leaves the Ag–P σ bonding orbital (impacts of Ag-40% and P-36%, Table S1) and locates on the intramolecular Ag-Ag bond, which is generated by the empty $5p_z$ orbitals of the silver cations. The vertical excitation energies for the three lowest triplets were 3.70, 4.30, and 4.60 eV (334, 287, and 269 nm), respectively. The first two triplets were of a LC^{NO3} nature, and the impact of metals and dpcym ligands appeared in the T₃ state. The T₃ had an excellent match to the S₂ state; their similarity was $s_H = 0.91$ and $s_E = 0.95$. Along with the oscillator strengths, this indicates a high probability for the excitation of 1 directly to S₂ state, S₂ \rightarrow T₃ interconversion, followed by the triplet emission from the T₃ state, which describes the emission observed (vide infra, Figure S13).



Figure 5. Highest occupied natural transition orbital (HONTO) and lowest unoccupied natural transition orbital (LUNTO) for the $S_0 \rightarrow S_2$ (**top**) and $S_0 \rightarrow T_3$ (**bottom**) transition in complex **1** as the isosurface at 0.05 a.u.

The excitation pattern of the complex $[Ag(Me_2Pz^H)(dppm)]_2(NO_3)_2$ (**2b**) differed from that observed for $[Ag(dcypm)]_2(NO_3)_2$ (**1**). The first singlet (4.16 eV, 298 nm, f = 0.2354; Figure 6) possessed a comparable impact to the hole from metals (35%) and phosphorus atoms (from dppm, 33%) with some contribution from 10% dimethylpyrazole (Figure S2, Table S2). However, the excited electron was located mainly on the organic part of the dppm ligand (64%), indicating the charge transfer character of this transition. Therefore, it could be ascribed to $(Ag^+ + P^{dppm} + N^{Pyrazole}) \rightarrow (Ph + CH_2)^{dppm}$ charge transfer. The electron density at the Ag…Ag intramolecular contact was still present in the excited S₁ state. Still, the contribution of Ag atoms to the excited state dropped by three times compared to the S₂ of complex **1**, and as a result, it could be observed only at the 0.03 a.u. isosurface (Figure S2). These data indicate the role of the dimethylpyrazole ligand in the metal-induced electronic transitions. The four lowest triplet states for **2b** were the ³LC states of Ph substituents in dppm ligands, while T₅ was the ³LC^{NO3} state (Figure S2). The T₆ of MLCT nature is the state coupled with the S₁ excitation, having high similarity (s_H = 0.91 and s_E = 0.90) to the S₀ \rightarrow T₆ transition energy 4.02 eV (308 nm) (Figure 6). Similar behavior was observed in the case of dinuclear silver pyrazolates with PCy₃ and PPh₃ ligands [35].

The TD-DFT analysis of $[Ag(dppm)]_2(Me_2Pz^H)(NO_3)_2$ (**2a**) excitations led to nearly the same pattern, except the disappearance of symmetry forbidden states, which led to doubling of the number of corresponding electronic transitions. At that, the S₁ and S₂ states both possess mixed MLCT (Ag⁺ + P^{dppm} + N^{Pyrazole}) \rightarrow (Ph + CH₂)^{dppm} + LC^{NO3} character with close excitation energies and oscillator strengths (4.11 eV, 301 nm, f = 0.0994 for S₁ and 4.17 eV, 297 nm, f = 0.1605 for S₂) as a result of mixing with symmetry forbidden A_G ¹LC^{NO3} state upon loss of symmetry (Figure 7, Table S3). Despite this mixing, the simulated excitation spectra were the same for **2a** and **2b** (Tables S2 and S3, Figure S3). For triplet transitions due to the unsymmetrical structure, the eight lowest triplets were ³LC states of Ph substituents in dppm ligands, and T₉-T₁₀ are ³LC^{NO3} states, while T₁₁ and T₁₂ were MLCT states. Due to the mixing of singlet states with LC^{NO3} transition, the discussed singlet and triplet states had a low similarity. Still, if we ignore the NO₃ group's contributions, the similarity for S₂-T₁₁ was s_H = 0.83, s_E = 0.79 and for S₂-T₁₂ it was s_H = 0.84, s_E = 0.75. Based on these, practically the same conclusion can be made as for **2b**. The lowest singlet excitation should lead to the high energy triplets T₁₁-T₁₂ that is likely to interconvert to the lower ³LC states of dppm' Ph substituents, which in turn has a trend to non-emissive relaxation at room temperature [35–37], but could be stabilized at 77 K.



Figure 6. HONTO and LUNTO for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_6$ in complex **2b** as the isosurface at 0.05 au.



Figure 7. HONTO and LUNTO for the $S_0 \rightarrow S_2$ and $S_0 \rightarrow T_{11}$ in complex **2a** as the isosurface at 0.05 au.

The UV–Vis spectra of **1** and **2a** were measured in CH₂Cl₂ (Figure 8). Complex **1** demonstrated an intense absorbance band at 267 nm ($\varepsilon = 13350 \text{ cm}^{-1} \text{ M}^{-}$). This band can be attributed to the transition with a metal-centered (MC) character originating from intramolecular Ag(I)–Ag(I) interactions [9]. The presence of the nitrate anion in complex **1** resulted in the non-intensive tail around 300 nm, which correlated with the absorption spectrum of the aqueous solution of silver nitrate.



Figure 8. Absorption spectra of complexes 1 (blue) and 2a (red) in CH₂Cl₂ solution.

UV–Vis spectrum of compound **2a** showed a broad, intense band at 288 nm ($\varepsilon = 12800 \text{ cm}^{-1} \text{ M}^{-1}$) with a long tail at ca. 335 nm, which can be assigned to the charge-transfer (MLCT or LLCT) transitions. Additionally, in the high energy region (<280 nm), weakly resolved bands with the contribution from several bands of close energies were observed. This band could be assigned only to the transitions of the $\pi \rightarrow \pi^*$ character within the Ph substituents in bisphosphine and pyrazole ligands.

The emission spectra of complexes 1 and 2a were studied in CH_2Cl_2 solution and the solid state (Figure 9). The room temperature (RT) emission spectrum of complex 1 in the solution displayed two bands at 370 and 390 nm, respectively, which can be assigned to the emission from the electronically excited states of MC nature. The emission bands of 1 in the solid state were in the same position. Temperature decrease led to the non-significant redistribution of the solid sample band's intensities. The triplet state decays also demonstrate this mixed emissive behavior. The phosphorescence decay of 1 both in the solution and in solid state at RT and 77 K can only be fitted with bi-exponential function. In the CH_2Cl_2 solution at RT, lifetimes were 1 and 10 μ s. In the solid state lifetimes, τ was practically independent of temperature being ca. 2 and 16 µs. These data demonstrate that complex 1 possessed the same photoluminescence both in solution and solid state. Complex 2a in the acetonitrile solution possessed phosphorescence bands at 365 and 410 nm (for both $\tau = 8.7 \ \mu s$). In the solid state at RT, complex **2a** showed an unstructured band at 380 nm of CT nature ($\tau = 9 \mu s$). Interestingly, at 77 K, the presence of a new intense band at 440 nm was observed ($\tau = 37 \ \mu s$). The position of the band observed at RT shifted from 380 to 390 nm at 77 K, but the lifetime of this emission was not dependent on the temperature (8.9 μ s). The results of calculations (vide supra) showed that the T₁-T₈ states were of LC nature within Ph substituents. As we have shown for structurally similar silver pyrazolate/dppm complexes, these states are not emissive due to the intersection of their energy surface with the ground state, which allows effective non-radiative relaxation [35–37]. The emission observed at 298 K can be ascribed to the system relaxation from T_{11-12} (3.98–4.21 eV) and higher states of ((M + L^{P+N})L^{dppm}CT) nature. The temperature decrease led to the stabilization of triplet states of the LC^{Ph} nature and these channels possess a main influence on the emission of 2a observed at 77 K.



Figure 9. Normalized emission ($\lambda_{exc} = 320 \text{ nm}$) spectra of complexes **1** (solid line) and **2a** (dashed line) in the solution (black) and solid state at 298 K (red) and 77 K (blue).

4. Conclusions

The reaction of silver nitrate with bisphosphines in the presence of 3,5-dimethylpyrazole gave new examples of dinuclear silver(I) complexes of different composition [Ag(dcypm)]₂(NO₃)₂ (1), $[Ag(dppm)]_2(NO_3)_2(Me_2Pz^H)$ (2a), and $[Ag(Me_2Pz^H)(dppm)]_2(NO_3)_2$ (2a). This suggests that the steric repulsion of bulky cyclohexyl substituents does not allow coordination of additional pyrazole ligand to the silver atoms in $[Ag(dcypm)]_2(NO_3)_2$. Complex **2a** was obtained by the crystallization of 2b from a diluted solution in accordance with low solubility accompanied by the elimination of one pyrazole molecule. For all complexes, non-typical κ^1 coordination of the nitrate anion was observed, which led to a significant distortion of the central eight-member cycle [AgPCP]₂ in comparison to related silver bisphosphine complexes. Complexes possessed phosphorescence both in the solution and in the solid-state. The intramolecular argenthophilic interaction observed in complex 1 (d(Ag...Ag) = 2.981 Å) introduces the main excitation channel in which an electron leaves the Ag-P bond orbital and locates on the intramolecular Ag-Ag bond (metal-centered character). The coordination of dimethylpyrazole to Ag(I) in complex 2a led to the elongation of the Ag. Ag distance (3.218 Å). Complex 2a exhibited a phosphorescence originating from the charge-transfer from the ${}^{3}(M + L^{P+N})L^{Ph}CT$ state at room temperature. At 77 K, the emission was split into two components: ${}^{3}(M + L^{P+N})L^{Ph}CT$ and ${}^{3}LC^{Ph}$ transitions. According to the TD-DFT calculations, the coordination of dimethylpyrazole to the metal atom mainly affects the energy of transition.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/10/881/s1, Figure S1: Natural transition orbital's of **1** as the isosurface at 0.05 a.u.; Table S1: Computed characteristics of the excited states of **1**. For analysis of fragment impacts (in %) to the ground state (hole) and excited state (electron), complex was divided to fragments of all Ag atoms, all P atoms, nitrate anions, and all atoms of dcypm ligand except P.; Figure S2: Natural transition orbital's of **2** as the isosurface at 0.05 a.u. except for S1 and T6; Table S2: Computed characteristics of the A_u symmetry excited states of **2**. For analysis of fragment impacts (in %) to the ground state (hole) and excited state (electron), the complex was divided to fragments of all Ag atoms, all P atoms, nitrate anions, pyrazolates, and all atoms of dppm ligand except P.; Figure S3: Natural transition orbital's of **2a** as the isosurface at 0.05 a.u., Table S3. Computed characteristics of the AU symmetry excited states of **2a**; Figure S4: Phosphorescence decay by delay of complex **1** at RT in CH₂Cl₂ solution (left) and solid state (right); Figure S5: Phosphorescence decay by delay of complex **1** in the solid state at 77 K; Figure S7: Phosphorescence decay by delay of complex **2a** at RT in CH₂Cl₂ solution (left) and solid state (right); Figure S4: Phosphorescence decay by delay of complex **1** in the solid state (at 77 K; Figure S7: Phosphorescence decay by delay of complex **2a** at RT in CH₂Cl₂ solution (left) and solid state (right); Figure S6: Phosphorescence decay by delay of complex **1** in the solid state (right); Figure S8: Phosphorescence decay by delay of complex **2a** at RT in CH₂Cl₂ solution (left) and solid state (right); Figure S8: Phosphorescence decay by delay of complex **2a** in the solid state at 77 K (measured at 390 nm); Figure S8: Phosphorescence decay

by delay of complex **2a** in the solid state at 77 K (measured at 440 nm); Figure S9: The ¹H NMR spectrum of complex **1** in CD₂Cl₂; Figure S10: The ³¹P{¹H} NMR spectrum of complex **1** in CD₂Cl₂; Figure S11: The 1H NMR spectrum of complex **2a** in CD₃CN; Figure S13: Schematic Jablonski diagram for **1**, **2a**, **2b**. Presumably active states indicated by solid lines; Figure S14: Comparison of X-ray and DFT geometry of Ag₂P₄(NO₃)₂ core for **1**, **2a** and **2b**. Atoms of X-ray structure is shaded, DFT structure is colored. Ag—cyan, P—orange, C—gray, O—red, N—blue; Figure S15: Excitation spectra of **1** in CH₂Cl₂ solution (left, em. on 370 and 390), and in the solid state (right, em. 370); Figure S16: Excitation spectra of **2a** in CH₂Cl₂ solution (left, em. on 410) and in the solid state (right, em. on **32**). Figure S17: IR spectrum of complex **2a** in KBr pellets; Figure S18: The simulated electronic spectra of **1**, **2a**, and **2b**. The 200 lowest energy singlet transitions were considered, and full width at half maximum was set to 40; Figure S19: ¹H NMR spectrum of the precipitate obtained in the case of interaction silver nitrate with dppm and Me₂Pz^H, demonstrating Ag/(Me₂PzH)/dppm = 1/1/1 ratio, CD₂Cl₂; Figure S20: ¹H NMR spectrum of the precipitate obtained in the case of interaction silver nitrate with dppm and Me₂Pz^H, demonstrating Ag/(Me₂PzH)/dppm = 1/1/1 ratio, CD₂Cl₂; Figure S20: ¹H NMR spectrum of the precipitate with dppm and Me₂Pz^H, demonstrating Ag/(Me₂PzH)/dppm = 1/1/1 ratio, CD₂Cl₂; Figure S20: ¹H NMR spectrum of the precipitate obtained in the case of interaction silver nitrate with dppm and Me₂Pz^H, demonstrating Ag/(Me₂PzH)/dppm = 1/1/1 ratio, CD₂Cl₂; Figure S20: ¹H NMR spectrum of the precipitate obtained in the case of interaction silver nitrate with dppm and Me₂Pz^H, demonstrating Ag/(Me₂PzH)/dppm = 1/1/1 ratio, CD₂Cl₂; Figure S20: ¹H NMR spectrum of the precipitate obtained in the case of interaction silver nit

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