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Mononuclear (N^N)(P^P) silver(I) complexes based on 2-(pyrazol-3-yl)pyridines and DPEphos

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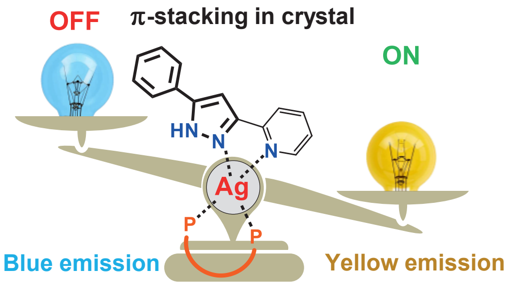
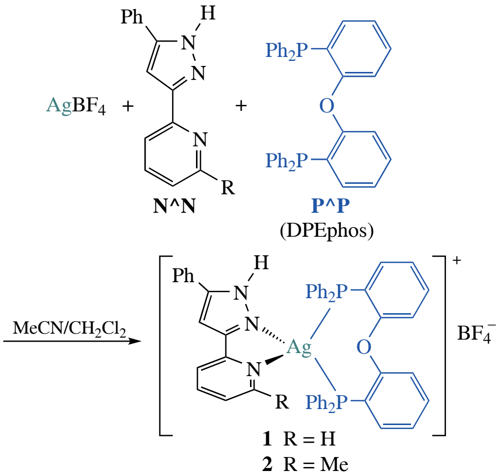
Mononuclear silver(I) (N^N)(P^P) complexes have been synthesized with 2-(5-phenyl-1*H*-pyrazol-3-yl)pyridine or its 6-methyl homologue and DPEphos as the ligands. The non-solvated complexes exhibit typical ligand-centered phosphorescence in the solid state, which is typical for silver(I) complexes with N^N aromatic chelating ligands. However, the presence of intermolecular π–π interactions between the N^N ligands in the solvated complexes leads to the formation of crystals which exhibit unstructured yellow phosphorescence.



Keywords: 2-(pyrazol-3-yl)pyridine, pyrazolate complexes, silver(I) compounds, chelating ligand, crystal structure, photoluminescence.

The design and synthesis of luminescent transition metal complexes has garnered significant attention in recent years due to their wide range of potential applications in optoelectronics, sensing, and photochemical catalysis.[1–4] Silver(I) complexes in particular are of interest due to their versatile coordination chemistry, tunable photophysical properties, and relatively low cost compared to gold(I) and platinum(II)[5] ones. Silver(I) complexes often exhibit rich coordination chemistry and photoluminescent behavior, which can be fine-tuned by the choice of ligands and geometry of the coordination environment.[6–12] The combination of nitrogen- and phosphorus-based ligands offers a promising approach to producing stable and luminescent group 11 metal complexes with customized properties.[13–16] Recently, on the example of pyridine–pyrazole Cu^I complexes, we have demonstrated the role of chelating bisphosphine on the efficiency of photoluminescence.[17] This study focuses on the synthesis and characterization of mononuclear silver(I) complexes featuring the chelating N^N ligands such as 2-(5-phenyl-1*H*-pyrazol-3-yl)pyridine and 6-methyl-2-(5-phenyl-1*H*-pyrazol-3-yl)pyridine, as well as DPEphos (Scheme 1). The (pyrazol-3-yl)pyridine derivatives have a rigid aromatic framework with a chelating pyrazole–pyridine motif providing a stable N^N coordination environment.[18] Ligand DPEphos should enhance electronic and steric properties of the complex. Complexes **1** and **2** were obtained by consequential reaction of $AgBF_4$ with a N^N derivative in the CH_2Cl_2/MeCN mixture with further addition of DPEphos.



Scheme 1

The reaction of $AgBF_4$ in CH_2Cl_2 with (pyrazolyl)pyridines followed by the addition of chelating bisphosphines leads to the formation of three types of complexes. The main quantity corresponds to the desired mix-ligand $[Ag(N^\wedge N)(P^\wedge P)]^+$ complex; however, significant amounts of $[Ag(P^\wedge P)_2]^+$ and $[Ag(N^\wedge N)_2]^+$ complexes are also formed. To prevent the formation of by-products, we found that it was necessary to first generate *in situ* the $AgBF_4$ complex with MeCN by adding the solvent to cause full dissolution of the initial salt before addition of CH_2Cl_2 and ligands. It should be noted that this procedure does not guarantee a pure product, and additional crystallization is required. Interestingly, crystals of complexes **1** and **2** suitable for X-ray diffraction were only obtained from CH_2Cl_2 solutions using hexane as a precipitating solvent. Both complexes are mononuclear with a distorted tetrahedral environment around the Ag ion.

Complex **1** without methyl group in the pyridine fragment crystallizes with four CH_2Cl_2 molecules per one metal complex in a crystal [formulated as $\mathbf{1}\cdot 4(CH_2Cl_2)$, Figure 1]. One of these solvent molecules forms a hydrogen bond with the fluorine atom of the BF_4 anion, while the others are stabilized only by weak H–H, H–F, and H–π contacts.[†] In the crystal, complexes form

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[†] *Crystal data for* $\mathbf{1}\cdot 4(CH_2Cl_2)$. $C_{54}H_{47}AgBCl_8F_4N_3OP_2$, monoclinic, space group $P2_1/n$, $a = 18.3419(11)$, $b = 12.3602(8)$ and $c = 25.6881(15)$ Å, $\alpha = \gamma = 90°$, $\beta = 107.576(3)°$, $V = 5551.9(6)$ Å^3, $Z = 4$, $d_{calc} = 1.548$ g cm^{-3}, $\mu = 0.862$ mm^{-1}, $R_1 = 0.0678$ [from 10898

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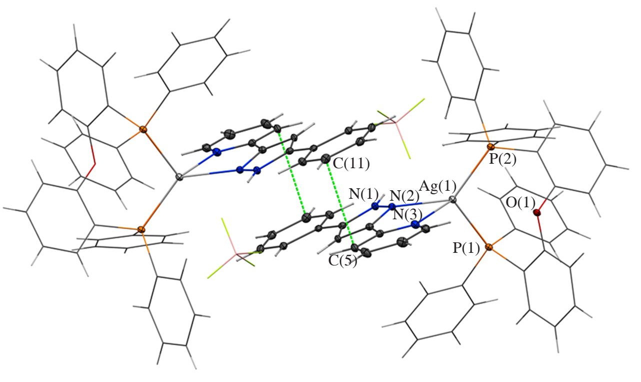

Figure 1 X-ray structure of a complex $\mathbf{1}\cdot4(CH_2Cl_2)$ dimer in a crystal. Selected interatomic distances (Å) and angles (°): Ag(1)–P(1) 2.489(1), Ag(1)–P(2) 2.411(2), Ag(1)–N(2) 2.321(5), Ag(1)–N(3) 2.371(6), N(1)–N(2) 1.345(7), C(5)–C(11) 3.368(9), N(2)–Ag(1)-N(3) 71.2(2), N(3)–Ag(1)–P(1) 114.3(1), and N(2)–Ag(1)–P(2) 134.9(1).

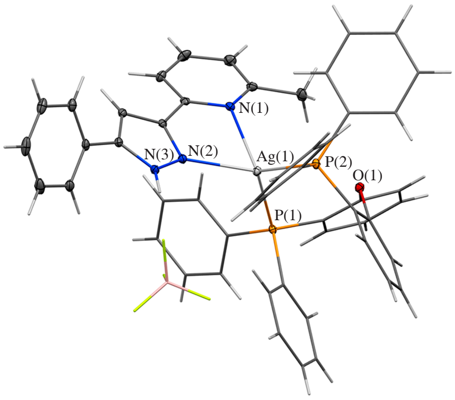

Figure 2 X-ray structure of complex **2** in a crystal. Selected interatomic distances (Å) and angles (°): Ag(1)–P(1) 2.4920(8), Ag(1)–P(2) 2.4341(8), Ag(1)–N(2) 2.332(2), Ag(1)–N(1) 2.432(2), N(3)–N(2) 1.352(3), N(1)–Ag(1)–N(2) 71.42(8), N(1)–Ag(1)–P(1) 105.25(6) and N(2)–Ag(1)–P(2) 120.66(6).

dimers *via* π–π interactions (the shortest C···C contact is 3.368 Å) and hydrogen bonds formed by fluorine atoms of the BF_4 anion with CH and NH groups. The fragments Pz–Py–Ph are practically planar. Complex $\mathbf{1}\cdot4(CH_2Cl_2)$ contains four CH_2Cl_2 molecules in a crystal structure; however, three of these solvent molecules can be easily removed by vacuum drying at 15 Torr as confirmed by elemental analysis for thus obtained $\mathbf{1}\cdot CH_2Cl_2$. The remaining solvent molecule can be removed only at higher vacuum (*ca*. 0.02 Torr) upon additional ultrasonic irradiation. The purity of this CH_2Cl_2-deprived complex **1** was also confirmed by elemental analysis; however, crystals of this substance suitable for X-ray diffraction analysis could not be grown. All further photophysical studies were performed using complex $\mathbf{1}\cdot CH_2Cl_2$, which contained one CH_2Cl_2 molecule, and complex **1**, which did not contain any solvent molecules.

In contrast, the crystal of complex **2** does not contain solvent molecules, which is responsible for the main differences in crystal packing compared to compound **1** (Figure 2).† There are no π–π interactions or other pathways for dimer formation in a crystal, which results in the loss of planarity of the pyrazolyl–pyridine fragment and the distortion of the N–Ag–N fragment. The angle between the planes of the Pz and Py moieties is 24.01°, whereas the same parameter for $\mathbf{1}\cdot4(CH_2Cl_2)$ is 12.04°. Moreover, there is no conjugation between the Pz and Ph fragments, as indicated by the angle of 43.23° between their planes. The bond lengths are similar in both complexes. Complex **2** being prepared does not require additional purification.

All complexes in the solid state at room temperature exhibit light emission (Figure 3). The nature and maxima of the observed emission depend on the crystal structure and the presence of solvent molecules. Complexes **1** and **2** display broad slightly structured bands in the blue-green region, with maxima around 490 nm. For complex **1**, τ is 35.8 μs, and for complex **2** it is 30 μs. Microsecond emission lifetimes indicate phosphorescence nature of the emission observed for both complexes. Complex $\mathbf{1}\cdot CH_2Cl_2$ in the solid state at room temperature (298 K) demonstrates the broad structureless band in the yellow region with a maximum at 540 nm and lifetime τ = 51.1 μs. There are structured bands with maxima at 433, 463, and 490 in the spectra of **1** and **2** at 77 K, which are typical of silver(I) complexes with aromatic N^N ligands.[14,19,20] These bands could be assigned to the ligand-centered emission (LC, *vide infra*). In contrast, the spectrum of $\mathbf{1}\cdot CH_2Cl_2$ shows a structureless band with maxima at *ca*. 550 nm even at 77 K. The emission behavior of this compound could be explained by the formation of excited exciplexes due to the π–π stacking interactions between pyrazolyl–pyridine ligands in neighboring molecules.[20–22] Based on the fact that differences in the photophysics of complexes may arise from differences in crystal packing, we attempted to rule out the possibility of intermolecular interactions. For this purpose, complex **1** was incorporated into a poly(methylmethacrylate) ($\mathbf{1}\cdot$PMMA) matrix at a weight fraction of 4%. This was done using a highly diluted CH_2Cl_2 solution, with further and slow solvent evaporation. The spectrum of $\mathbf{1}\cdot$PMMA at 298 K shows a structured band with maxima at 432, 458, and 486 nm and a shoulder at *ca*. 530 nm (τ = 95.1 ms) that is similar to that observed for solids **1** and **2**. A decrease in temperature to 77 K results in the appearance of a higher structured emission at 427, 454, and 481 nm, and 517 nm. The similarity in emission profiles and maxima positions indicates the identity of the excited states, confirming the preference for LC emission for non-solvated complexes in the solid state and the importance of intermolecular interactions for the emission of $\mathbf{1}\cdot CH_2Cl_2$.

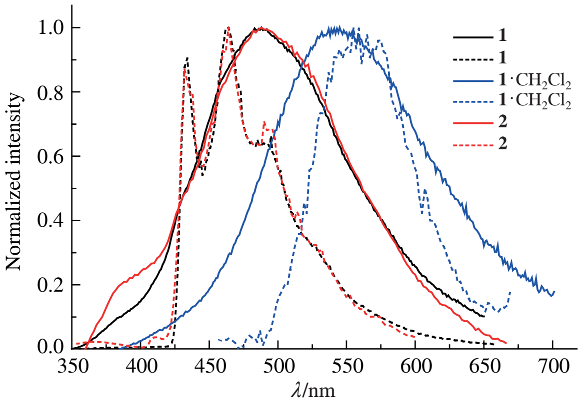

Figure 3 Photoluminescence spectra of complexes **1** and **2** in the solid state at 298 K (solid lines) and 77 K (dashed lines).

TD-DFT calculations (ωB97X-D3 functional and the ZORA-TZVP/SARC-ZORA-TZVP basis set) of vertical excitations of complexes **1** predict that the lowest singlet

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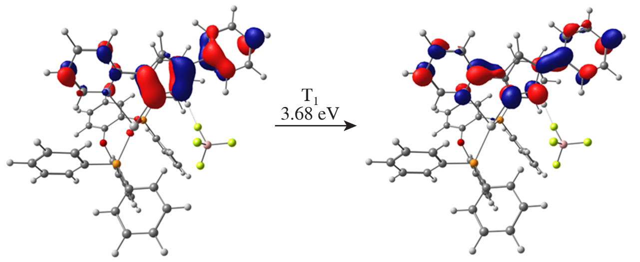
unique reflections with $I > 2\sigma(I)$] and $wR_2 = 0.2091$ (from all 50657 unique reflections).

Crystal data for **2**. $C_{51}H_{41}AgBF_4N_3OP_2$, monoclinic, space group $P2_1$, $a = 9.7804(4)$, $b = 16.7939(7)$ and $c = 13.9098(6)$ Å, $\alpha = \gamma = 90°$, $\beta = 102.3910(10)°$, $V = 2231.48(16)$ Å^3, $Z = 2$, $d_{calc} = 1.441$ g cm^{-3}, $\mu = 0.582$ mm^{-1}, $R_1 = 0.0204$ [from 8705 unique reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0467$ (from all 21332 unique reflections).

CCDC 2441179 and 2441180 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.



HONTO LUNTO

Figure 4 Natural transition orbitals HONTO and LUNTO for the $S_0 \rightarrow T_1$ excitation of complex **1** as an isosurface at 0.05 a.u.

(4.70 eV) is a $^{1}(\mathrm{M+P})\mathrm{L}^{\mathrm{N^\wedge N}}\mathrm{CT}$ transition involving d-orbitals of the Ag ion and σ-orbitals of phosphorus atoms in DPEphos (see Online Supplementary Materials). The lowest triplet state (3.68 eV) has a different nature, consisting of $\pi \rightarrow \pi^*$ transitions (LC, Figure 4), which are typical for the complexes of chelating N^N ligands with Ag ions. These data are in good agreement with the spectral behaviour for non-solvated **1**, **2**, and **1**·PMMA, demonstrating the preference for these emissions.

In conclusion, we have described three new mononuclear silver(I) complexes with chelating 2-(5-phenyl-1*H*-pyrazol-3-yl)-pyridine derivatives and DPEphos. Crystallization of complex **1** from CH_2Cl_2 leads to the formation of dimers *via* π–π intermolecular interactions. However, the presence of the Me substituent on the pyridine moiety prevents these interactions, resulting in a loss of planarity of the N^N ligand. Complex **1**·CH_2Cl_2, which exhibits intermolecular stacking interactions shows emission that can be attributed to the formation of excited exciplexes. The lack of these interactions (due to grinding, drying, or the use of a PMMA matrix) leads to emission of typical N^N-P^P silver complexes exhibiting ligand-centered phosphorescence in the solid state.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7797.

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