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Synthesis, structures and photophysical properties of phosphorus-containing silver 3,5-bis(trifluoromethyl)pyrazolates

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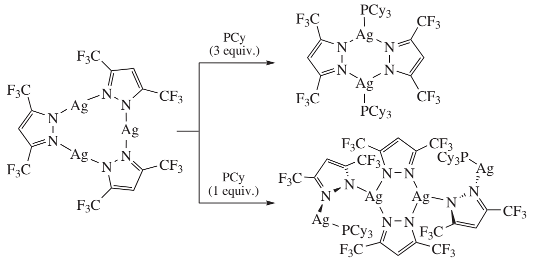
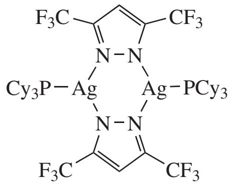
Reaction of a trinuclear silver pyrazolate $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ complex with tricyclohexylphosphine at different reagent ratios leads to the formation of heteroleptic dinuclear or tetranuclear complexes. According to the single crystal X-ray analysis of the dinuclear complex, hexane molecules are incorporated into the cavities formed as the result of supramolecular packing. Coordination of a phosphine ligand makes dinuclear silver pyrazolate to exhibit blue emission at room temperature.



Pyrazolates are common building blocks in coordination chemistry and crystal engineering. Cyclic silver pyrazolates take special place in this chemistry because of their appealing luminescent properties and capability of forming supramolecular aggregates due to acid/base or metallophilic interactions.[1–5] Recently, we have demonstrated that design of macrocyclic supramolecular aggregations can be realized *via* complexation of macrocyclic pyrazolates with bases of different nature: π-electron ligands of the sandwich compounds,[6,7] keto groups and boron hydrides.[8] The implementation of phosphine ligand in the eleventh group metal complexes entails long luminescence lifetimes in both solid state and frozen solution.[9] Despite that silver complexes containing both N- and P-ligands have the high potential in terms of their photophysical properties,[10–13] examples of phosphorus-containing silver pyrazolate complexes are still rare.[14] In the course of our ongoing investigation of the macrocyclic silver pyrazolates and their interaction with electron donors, we have discovered that the reaction of trinuclear silver pyrazolate $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ **1** (Pz = pyrazolate) with tricyclohexylphosphine (PCy_3) in toluene at room temperature yields complexes of different structure depending on the stoichiometry. For example, a stoichiometric reaction (one PCy_3 per one silver atom) leads to the formation of dinuclear complex $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_2(PCy_3)_2$ **2**,[15] while an increase of the macrocycle **1** amount (one trinuclear macrocycle per one PCy_3) results in tetranuclear complex $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_4(PCy_3)_2$ **3**.[†] Interestingly, trinuclear structures were not observed under any conditions.

The molecule of complex **2** in the crystal is located on a two-fold axis centered at the Ag_2N_4 (Figure 1).[‡] Coordination of the PCy_3 moiety leads to a significant elongation of the Ag–N bonds to 2.212–2.343 Å in the molecule of **2** relative to 2.081–2.096 Å in the parent trinuclear silver macrocycle.[3] The orientation of the substituents provides the efficient minimization of the steric repulsions of the bulky phosphine. The core Ag_2N_4 moiety has twisted boat conformation in contrast to the reported planar dinuclear silver complex with non-substituted pyrazolate ligand and PPh_3.[14] The modes of bidentate bridging coordination of both pyrazolate ligands to the silver atoms are not similar: Ag(1) atom is out of the $N_2C_3^{Pz}$ planes by 0.126–0.432 Å.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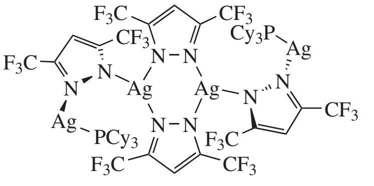
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The crystal structure data revealed the inclusion of one hexane molecule per one molecule of **2**, which was found in the intermolecular cavities formed as the result of supramolecular packing (Figure 2). The shortest intermolecular H–H and H–F distances are 2.571 and 2.750 Å, respectively, that is longer than the sum of Van der Waals radii. This suggests the absence of intermolecular Van der Waals interactions between the solvent molecule and the macrocycle.

[†] *General procedure*. Mixtures of trinuclear silver pyrazolate **1** (0.0536 mmol) and the corresponding amount of tricyclohexylphosphine (0.01608 mmol for **2** and 0.0536 mmol for **3**) in 3 ml of anhydrous benzene were stirred overnight at room temperature under Ar atmosphere. The solvent was evaporated to dryness under reduced pressure. White products were recrystallized from anhydrous boiling hexane by immediate cooling to 0 °C.

[‡] Colorless crystals of complexes **2** and **3** suitable for the X-ray analysis of single crystal were obtained from the equimolar CH_2Cl_2/hexane solution by slow solvent evaporation in a refrigerator (at +4 °C).

Crystal data for **2**: $C_{46}H_{70}Ag_2F_{12}N_4P_2$, monoclinic, space group C_2/c, $a = 20.7067(11)$, $b = 14.8154(8)$ and $c = 20.6394(12)$ Å, $\beta = 114.5200(10)°$, $V = 5760.7(6)$ Å^3, $Z = 8$, $d_{calc} = 1.463$ g cm^{-3}, $\mu = 8.11$ cm^{-1}, $R_1 = 0.0361$ [from 7702 unique reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0694$ (from all 61760 unique reflections).

Crystal data for **3**: $C_{56}H_{70}Ag_4F_{24}N_8P_2$, triclinic, space group $P\bar{1}$, $a = 11.269(2)$, $b = 12.710(3)$ and $c = 13.624(3)$ Å, $\alpha = 63.96(3)°$, $\beta = 78.31(3)°$, $\gamma = 77.24(3)°$, $V = 1697.5(8)$ Å^3, $Z = 1$, $d_{calc} = 1.765$ g cm^{-3}, $\mu = 12.92$ cm^{-1}, $R_1 = 0.0246$ [from 9190 unique reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0588$ (from all 22507 unique reflections).

CCDC 1827760 and 1827761 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

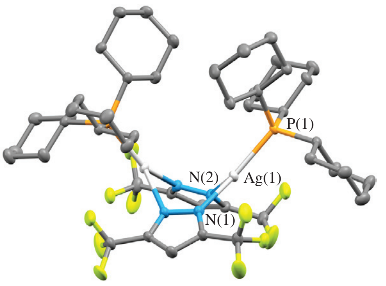

Figure 1 Molecular structure of complex **2** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ag(1)–P(1) 2.3662(6), Ag(1)–N(1) 2.212(2), Ag(1)–N(2) 2.343(1), N(1)–N(2) 1.355(2). Selected dihedral angle: [P(1)N(1)N(2)]/[N(1)N(2)N(2A)N(1A)] 50.67°.

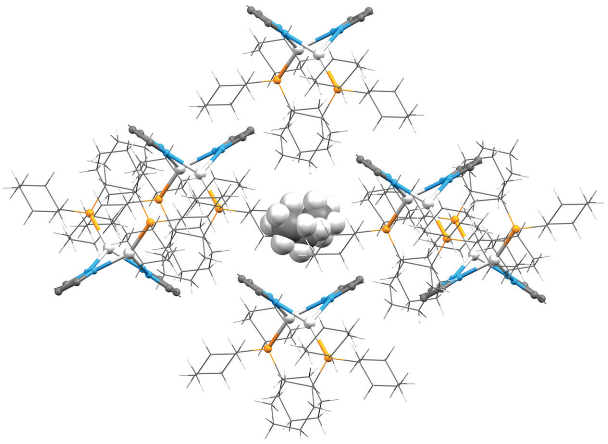

Figure 2 The fragment of **2** supramolecular packing (Ag, P, and Pz are depicted as balls and sticks, while wireframes represent Cy) showing environment around hexane molecule (spacefill).

The molecule of complex **3** in the crystal is in a special position and is located on the inversion center of the Ag_2N_4 (Figure 3). The Ag(1)–N(1) bond is shorter by 0.075–0.118 Å than the bonds of Ag(2) with three coordinated nitrogen atoms. The Ag(1)–P(1) bond length of 2.362 Å is similar to that in the molecule of complex **2**. The central metal-nitrogen cycle is fully symmetric (has local C_s symmetry) and is practically planar. The carbon atoms of the pyrazolate rings are slightly exposed out from the plane of the central Ag_2N_4 ring by only 0.108–0.232 Å. This deviation is only slightly smaller than that for the silver dimer with the non-substituted pyrazolate and triphenylphosphine.[14]

The photoluminescence of the dinuclear pyrazolate **2** was studied in the solid state. It was previously shown that trinuclear silver 3,5-bis(trifluoromethyl)pyrazolate possesses blue luminescence only at low temperatures (<77 K).[3] The present work revealed that the coordination of phosphorus-containing bases provides light emission also at room temperature. The UV excitation at short wavelengths ($\lambda \leqslant 300$ nm) is required to generate the blue emission bands (λ_{max} = 480 nm) at 298 K (Figure 4). The compound exhibits a non-significant luminescence thermochromism. Its emission band shifts by 10 nm to the blue region upon the temperature decrease to 77 K.

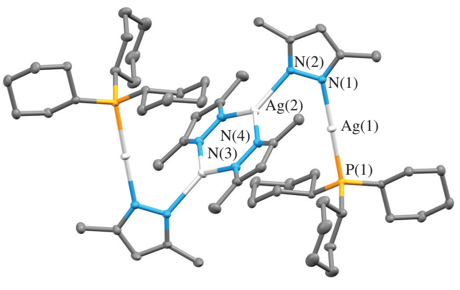

Figure 3 Molecular structure of complex **3** showing thermal ellipsoids at the 50% probability level (hydrogen and fluorine atoms are omitted). Selected bond lengths (Å): Ag(1)–P(1) 2.362(1), Ag(1)–N(1) 2.138(2), Ag(2)–N(3) 2.213(2), Ag(2)–N(2) 2.250(2), Ag(2)–N(4) 2.256(2).

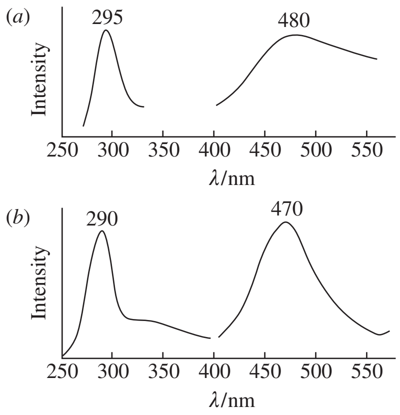

Figure 4 Photoluminescence spectra of crystals of **2** at (*a*) room temperature and (*b*) 77 K.

In summary, we have demonstrated that dinuclear silver pyrazolates could be prepared by the reaction of corresponding trinuclear analogue with tertiary alkylphosphine. The variation of reaction conditions can afford not only dinuclear, but also tetranuclear structures. The presence of bulky cyclohexyl substituents makes supramolecular packing less dense and leads to the formation of cavities. Being of the appropriate size hexane molecules become confined inside the cavity at least in the case of dinuclear pyrazolate. The coordination of tertiary phosphine makes silver pyrazolate photoluminescenting in solid state at room temperature.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.07.015.

References

1 A. A. Mohamed, *Coord. Chem. Rev*., 2010, **254**, 1918.
2 H. V. Dias and C. S. Gamage, *Angew. Chem. Int. Ed*., 2007, **46**, 2192.
3 M. A Omary, M. A Rawashdeh-Omary, M. W. A. Gonser, O. Elbjeirami, T. Grimes, T. R. Cundari, H. V. K. Diyabalanage, C. S. P. Gamage and H. V. R. Dias, *Inorg. Chem*., 2005, **44**, 8200.
4 J.-H. Chen, Y.-M. Liu, J.-X. Zhang, Y.-Y. Zhu, M.-S. Tang, S. W. Ng and G. Yang, *CrystEngComm*, 2014, **16**, 4987.
5 R. Galassi, S. Ricci, A. Burini, A. Macchioni, L. Rocchigiani, F. Marmottini, S. M. Tekarli, V. N. Nesterov and M. A. Omary, *Inorg. Chem*., 2013, **52**, 14124.
6 O. A. Filippov, A. A. Titov, E. A. Guseva, D. A. Loginov, A. F. Smol'yakov, F. M. Dolgushin, N. V. Belkova, L. M. Epstein and E. S. Shubina, *Chem. Eur. J*., 2015, **21**, 13176.
7 A. A. Titov, A. F. Smol'yakov, A. N. Rodionov, I. D. Kosenko, E. A. Guseva, Ya. V. Zubavichus, P. V. Dorovatovskii, O. A. Filippov and E. S. Shubina, *Russ. Chem. Bull., Int. Ed*., 2017, **66**, 1563 (*Izv. Akd. Nauk, Ser. Khim*., 2017, 1563).
8 A. A. Titov, O. A. Filippov, L. M. Epstein, N. V. Belkova and E. S. Shubina, *Inorg. Chim. Acta*, 2018, **470**, 22.
9 D. G. Cuttell, S.-M. Kuang, P. E. Fanwick, D. R. McMillin and R. A. Walton, *J. Am. Chem. Soc*., 2002, **124**, 6.
10 V. W.-W. Yam, V. K.-M. Au and S. Y.-L. Leung, *Chem. Rev*., 2015, **115**, 7589.
11 H. Yersin, R. Czerwieniec, M. Z. Shafikov and A. F. Suleymanova, *ChemPhysChem*, 2017, **18**, 3508.

12 M. A. Rawashdeh-Omary, M. D. Rashdan, S. Dharanipathi, O. Elbjeirami, P. Ramesh and H. V. R. Dias, *Chem. Commun.*, 2011, **47**, 1160.
13 M. A. Omary, O. Elbjeirami, C. S. P. Gamage, K. M. Sherman and H. V. R. Dias, *Inorg. Chem.*, 2009, **48**, 1784.
14 G. A. Ardizzoia, G. La Monica, A. Maspero, M. Moret and N. Masciocchi, *Inorg. Chem.*, 1997, **36**, 2321.
15 G. A. Ardizzoia, S. Cenini, G. La Monica, N. Masciocchi, A. Maspero and M. Moret, *Inorg. Chem.*, 1998, **37**, 4284.
16 *APEX II Software Package*, Bruker AXS Inc., Madison, WI, 2005.
17 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.
18 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

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