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Luminescent silver nitrate complexes of bis[2-(diphenylphosphano)phenyl]ether (DPEphos): Crystal structure of $[Ag(DPEphos)(py2SH)_2]NO_3$

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Heteroleptic silver(I) nitrate complexes containing the bis[2-(diphenylphosphano)phenyl]ether (DPEphos) ligand and the heterocyclic thioamides pyridine-2(1H)-thione (py2SH), pyrimidine-2(1H)-thione (pymtH), 4,6-dimethylpyrimidine-2(1H)-thione (dmpymtH), 1,4,5,6-tetrahydropyrimidine-2-thione (thpymtH) or 1,3-imidazolidine-2-thione ($imtH_2$) have been synthesized and characterized by IR and UV–Vis spectroscopy, elemental analyses and melting point determinations. The complexes can be obtained by the addition of the thioamide ligand to an $AgNO_3$–diphosphane adduct in dichloromethane/ethanol solution. The molecular structure of $[Ag(DPEphos)(py2SH)_2]NO_3$ complex has been established by single-crystal X-ray diffraction. The structure features a tetrahedral silver(I) center with two phosphorus atoms from the chelating diphos ligand, and the exocyclic sulfur atom of two heterocyclic thioamide units. Intense blue-green emission is observed in the region 470–483 nm for all the complexes in the solid state and in solution at ambient temperature.

1. Introduction

In recent years, a large number of luminescent d^{10} metal complexes have been used as components for luminescent-based chemical sensors [1], as photocatalysts and photoinitiators [2], as dopants to increase the electroluminescence efficiency of organic light emitting diodes [3], or as sensitizers in solar-energy conversion [4]. In this respect, group 11 d^{10} metal complexes are beginning to receive particular attention, especially Cu^I complexes bearing polypyridine and phenanthroline luminophores [5], often combined with bis[2-(diphenylphosphano)phenyl]ether (DPEphos) as a second rigid chelating ligand [6]. In general, most of these group 11 metal complexes with interesting photoluminescence properties are di- or multinuclear species, whereas luminescence among their mononuclear counterparts is considerably less pronounced. In addition, luminescence within Ag^I complexes is observed at low temperatures rather than at room temperature [7].

It is established that the emissive exited state in most of the luminescent Cu^I complexes involves a metal-to-ligand charge transfer (MLCT). This process requires oxidation of the d^{10} ion, which is obviously unlikely to occur in the case of silver [8], thus emission in Ag^I complexes is believed to predominantly originate from cluster-centered (MC) or ligand-centered (IL) excited states [9]. On the other hand, in a recent study, the emission properties of three $AgNO_3$–bis(diphosphane) complexes have been investigated using various experimental and theoretical methods, whereby emission has been attributed to originate from two different excited states, namely IL + MLCT and MC, corresponding to a tetrahedral and a square-planar geometry, respectively [10].

Exploring the photochemistry of mixed-ligand monovalent group 11 metal complexes incorporating chelating phosphanes in the coordination sphere, we recently presented two series of luminescent Cu^I compounds formulated as [CuX(DPEphos)(thione)] (X = Cl, Br, I) and [Cu(κ^3-triphos)(thiolate)], respectively [11], with tunable emission energy. Aiming to further contribute to the understanding of the impact of the thione ligand on the luminescence properties of thione/phosphane mixed-ligand complexes, we wish in this work to report on new luminescent derivatives resulting from the reactions of silver(I) nitrate with DPEphos and some neutral heterocyclic thiones.

2. Experimental

2.1. Materials and instrumentation

Commercially available silver nitrate and bis[2-(diphenylphosphano)phenyl]ether were used as received while the thiones (Aldrich) were re-crystallized from hot ethanol prior to their use.

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All the solvents were purified by respective suitable methods and allowed to stand over molecular sieves. Infra-red spectra in the region of 4000–250 cm^{-1} were obtained in KBr discs with a Perkin-Elmer 1430 spectrophotometer, while a Perkin-Elmer–Hitachi 200 spectrophotometer and a Hitachi F-7000 Fluorescence Spectrophotometer were used to obtain the electronic absorption and emission spectra, respectively. Melting points were measured in open tubes with a STUART scientific instrument and are uncorrected. Molar conductivities, magnetic susceptibility measurements and elemental analyses for carbon, nitrogen and hydrogen were performed as described previously [11a].

2.2. Crystal structure determination

Single crystals suitable for crystal structure analysis were obtained by slow evaporation of an acetonitrile/ethanol solution of the complex at room temperature. X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD area-detector diffractometer. The programs DENZO [12] and COLLECT [13] were used in data collection and cell refinement. Details of crystal and structure refinement are compiled in Table 1. The structures were solved using program SIR97 [14] and refined with program SHELX-97 [15]. Molecular plots were obtained with program ORTEP-3 [16].

2.3. General procedure for the synthesis of complexes **1**–**5**

To a suspension of 85 mg (0.5 mmol) of silver nitrate in 40 cm^3 of dry acetonitrile, 269.3 mg (0.5 mmol) of (oxydi-2,1-phenylene)bis-(diphenylphosphine) was added and the mixture was stirred for 1 h at 50 °C, whereupon a white precipitate was formed, which was then treated with the appropriate thione (0.5 mmol) dissolved in a small amount (~20 cm^3) of ethanol. The new reaction mixture was stirred for additional 2 h at 50 °C and the resulting clear solution was allowed to evaporate at ambient affording a microcrystalline solid, which was filtered off and dried *in vacuo*.

*[Ag(DPEphos)(py2SH)$_2$]NO$_3$ (**1**).* Yellow crystals (344 mg, 74%), m.p. 198 °C; *Anal.* Calc. for $C_{46}H_{38}AgN_3O_4P_2S_2$: C, 59.36; H, 4.11, N: 4.51. Found: C, 59.41; H, 4.08; N, 4.49%. IR (cm^{-1}): 3446br, 3136w, 3050m, 1575s, 1559s, 1457s, 1435vs, 1385vs, 1302s, 1261s, 1220vs, 1093s, 1071s, 941m, 878m, 802m, 748vs, 698vs, 508s; UV–Vis [λ_{max} (nm), log ε], (CH_3CN): 222 (4.36), 287 (4.27), 367 (3.85); Λ_m (mho cm^2 mol^{-1}), (CH_3CN): 140.

*[Ag(DPEphos)(pymtH)$_2$]NO$_3$ (**2**).* Yellow crystals (396 mg, 85%), m.p. 204 °C; *Anal.* Calc. for $C_{44}H_{36}AgN_5O_4P_2S_2$: C, 56.66; H, 3.89; N, 7.51. Found: C, 56.88; H, 3.78; N, 6.98%. IR (cm^{-1}): 3433br, 3186w, 3047m, 2920m, 1619s, 1588vs, 1575vs, 1557vs, 1457m, 1432vs, 1381s, 1311s, 1214s, 1130vs, 1032s, 991m, 855s, 745s, 689s, 507m; UV–Vis [λ_{max} (nm), log ε], (CH_3CN): 203 (5.32), 288 (4.95), 371 (3.78); Λ_m (mho cm^2 mol^{-1}), (CH_3CN): 142.

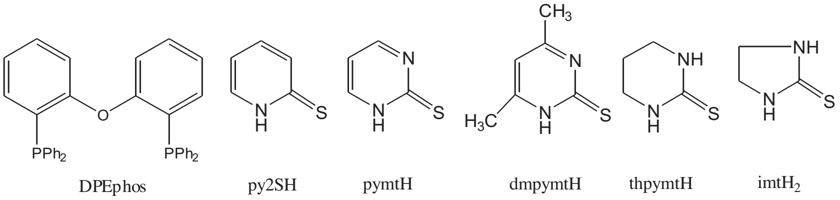
*[Ag(DPEphos)(dmpymtH)$_2$]NO$_3$ (**3**).* Yellow crystals (390 mg, 79%), m.p. 194 °C; *Anal.* Calc. for $C_{48}H_{44}AgN_5O_4P_2S_2$: C, 58.30; H, 4.48; N, 7.08. Found: C, 56.41; H, 4.55; N, 7.29%. IR (cm^{-1}): 3050m, 2920m, 1619s, 1568vs, 1457s, 1442vs, 1381s, 1299s, 1232vs, 1093s, 1023m, 976m, 875m, 796m, 748vs, 694vs, 508s, 454s; UV–Vis [λ_{max} (nm), log ε], (CH_3CN): 207 (4.39), 282 (3.98), 360 (2.95); Λ_m (mho cm^2 mol^{-1}), (CH_3CN): 139.

*[Ag(DPEphos)(thpymtH)$_2$]NO$_3$ (**4**). Colorless* crystals (386 mg, 82%), m.p. 230 °C; *Anal.* Calc. for $C_{44}H_{44}AgN_5O_4P_2S_2$: C, 56.17; H, 4.71; N, 7.44. Found: C, 55.67; H, 4.72; N, 7.51%. IR (cm^{-1}): 3226br, 3052m, 2959m, 1557vs, 1464s, 1439vs, 1379vs, 1303vs, 1228vs, 1090s, 1023m, 1067s, 872m, 809m, 747vs, 694vs, 507s, 471s; UV–Vis [λ_{max} (nm), log ε], (CH_2Cl_2): 252 (4.76), 286 (4.23); Λ_m (mho cm^2 mol^{-1}), (CH_3CN): 142.

*[Ag(DPEphos)(imtH)$_2$]NO$_3$ (**5**). Colorless* solid (338 mg, 74%), m.p. 224 °C; *Anal.* Calc. for $C_{42}H_{40}N_5AgO_4P_2S_2$: C, 55.27; H, 4.42; N, 7.67.

Table 1
Crystal data and structure refinements for [Ag(DPEphos(py2SH)$_2$]NO$_3$, (**1**).

Molecular formula	$C_{46}H_{38}AgN_3O_4P_2S_2$
Formula weight	930.72
T (K)	120(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	10.4278(2)
b (Å)	18.9311(2)
c (Å)	21.3928(3)
α (°)	90
β (°)	94.5580(10)
γ (°)	90
V (Å^3)	4209.79(11)
Z	4
D_{calc} (mg/m^3)	1.468
Absorption coefficient (mm^{-1})	0.702
F(000)	1904
Crystal size (mm)	0.28 × 0.20 × 0.17
θ (°)	3.06–27.47
Index ranges	$-11 \leqslant h \leqslant 13$
	$-23 \leqslant k \leqslant 24$
	$-27 \leqslant l \leqslant 27$
Reflections collected	47068
Independent reflections (R_{int})	9626 (0.0503)
Completeness	99.7% (θ = 27.47°)
Data/restraints/parameters	9626/0/518
Maximum and minimum transmission	0.8900 and 0.8277
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.035
Final R indices [$(I > 2\sigma(I))$]	$R_1 = 0.0347$, $wR_2 = 0.00762$
R indices (all data)	$R_1 = 0.0479$, $wR_2 = 0.0824$
Final weighting scheme	Calc. $w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 3.8436P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest difference in peak and hole (e Å^3)	0.574 and −0.661



Scheme 1. The diphosphane and heterocyclic thiones used as ligands with their abbreviations.

Found: C, 55.06; H, 4.27; N, 7.69%. IR (cm^{-1}): 3395s, 3065m, 2927m, 1579vs, 1481vs, 1432vs, 1392s, 1383s, 1303vs, 1250s, 1205vs, 1094m, 1027m, 918m, 872s, 724vs, 693vs, 531s, 511vs; UV–Vis [λ_{max} (nm), log ε], (CH_2Cl_2): 266 (4.87); Λ_m (mho cm^2 mol^{-1}), (CH_3CN): 149.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

Reaction of silver(I) nitrate with DPEphos and a heterocyclic thioamide ligand in dry dichloromethane/ethanol mixtures gives good yields of the complexes [Ag(DPEphos)(thione)$_2$]NO_3 (thione = pyridine-thione, pyrimidine-2-thione, 4,6-dimethylpyrimidine-2-thione, 1,4,5,6-tetrahydropyrimidine-2-thione and 1, 3-imidazolidine-2-thione) (Scheme 1).

The yellow to orange colored air- and moisture-stable microcrystalline solids are diamagnetic and soluble in common organic solvents like dichloromethane, chloroform and acetone. Their acetonitrile solutions behave as 1:1 electrolytes.

The electronic absorption spectra of compounds **1**–**5**, recorded in acetonitrile at room temperature, show two intense broad bands with maxima in the 275–290 and 380–398 nm regions, respectively. With reference to the absorption of the uncoordinated DPEphos (272 nm), the first one can be attributed to intraligand $\pi \rightarrow \pi^*$ transitions on the phenyl groups of the triphos ligand, whereby the lower energy band should be considered as a thione-originating intraligand transition, as it lies in the region where the free thiones absorb, expressing a small red shift as a consequence of the coordination to Cu^I.

The infrared spectra of compounds **1**–**5** contain, apart from the strong vibrational phosphane bands, which remain practically unshifted upon coordination, the characteristic four "thioamide bands" due to the presence of the heterocyclic thione ligands, with shifts indicative of an exclusive S-coordination mode, as well as a broad band in the 3430–3460 cm^{-1} region assigned to the ν(NH) stretching vibration. Ionic nitrate is indicated by the presence of a strong sharp band at ~1380 cm^{-1}.

3.2. X-ray structure

The single crystal structure of [Ag(DPEphos)(py2SH)$_2$]NO_3 (compound **1**) has been determined. An ORTEP view is shown in Fig. 1, and the coordination and geometrical parameters are listed in Table 2.

The Ag center possesses a distorted tetrahedral geometry surrounded by two P atoms of the DPEphos and two S atoms of two py2SH ligands. The P–Ag–P angle of the chelating diphosphane [112.20(2)°] is somewhat larger than the values of 106.37(2)° and 105.96(2)° found in [Ag(DPEphos)$_2$][OTf] [17], yet still clearly larger than its natural bite angle. Further conformational adaptation of the DPEphos backbone upon coordination involves widening of the angle between the phenyl rings by 21° to a value of ca. 82°, whereas the distance between the two P atoms becomes clearly shorter (4.1643(8) Å) compared to that found in the free DPEphos [4.876(1) Å].

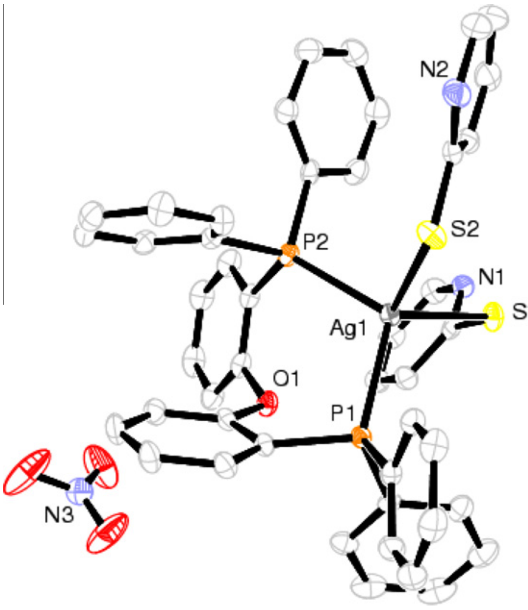


Fig. 1. A view of [Ag(DPEphos)(py2SH)$_2$]NO_3 (**1**) with atom labels. Displacement ellipsoids are shown in the 50% probability level.

The two Ag–P bond distances are 2.4856(6) and 2.5315(6) Å. respectively, slightly shorter than those found in [Ag(DPEphos)$_2$][OTf]. The Ag–S bond distances of 2.5437(6) and 2.5949(6) Å are somewhat shorter than the values previously found in complexes with a similar AgS_2P_2 structural core [18]. The non-bonding distance of 3.304 Å between the ether O atom and the Ag atom, only marginally larger than the sum of their van der Waals radii of ca. 3.24 Å, may have an influence on the structure of the complex. Additionally, as in many other silver nitrate complexes containing heterocyclic thione ligands, there is a network of hydrogen bonds in the crystal involving the O atoms of the anion and the N atoms of the two thione units.

3.3. Luminescence

The RT luminescence spectra of the complexes in the solid state have been studied. The absorption and emission spectrum of a representative compound **3** is shown in Fig. 2 while absorption and emission data of the complexes under investigation are summarized in Table 3. The RT luminescence spectrum of solid DPEphos consists of a broad band with maximum at 453 nm, whereas the emission maximum of [Ag(DPEphos)$_2$]NO_3 appears slightly blue-shifted (433 nm), suggesting the IL character of the emissive exited state, which is perturbed by the metal.

Compounds **1**–**3** exhibit an intense blue-green emission with λ_{max} values of the broad bands in 470–530 nm range when excited at λ = 350 nm at room temperature in the solid state, expressing

Table 2
Selected bond lengths (Å) and angles (°) for **1**.

Ag(1)–P(1)	2.4856(6)	S(1)–C(37)	1.706(2)
Ag(1)–P(2)	2.5315(6)	N(3)–O(3)	1.217(3)
Ag(1)–S(2)	2.5437(6)	N(3)–O(2)	1.233(3)
Ag(1)–S(1)	2.5949(6)	N(3)–O(4)	1.238(3)
S(1)–C(37)	1.706(2)		
P(1)–Ag(1)–P(2)	112.20(2)	C(37)–S(1)–Ag(1)	101.52(8)
P(1)–Ag(1)–S(2)	112.55(2)	C(42)–S(2)–Ag(1)	108.99(9)
P(2)–Ag(1)–S(2)	106.13(2)	O(3)–N(3)–O(2)	123.7(3)
P(1)–Ag(1)–S(1)	109.59(2)	O(3)–N(3)–O(4)	118.0(3)
P(2)–Ag(1)–S(1)	111.26(2)	O(2)–N(3)–O(4)	118.2(3)
S(2)–Ag(1)–S(1)	104.85(2)		

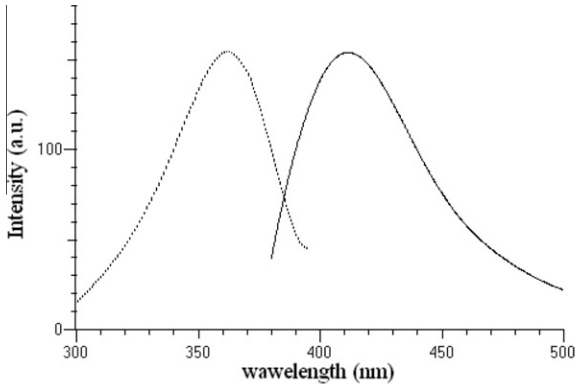


Fig. 2. Room temperature excitation and emission spectrum of [Ag(DPEphos)(dmpymtH)$_2$]NO$_3$ (**3**) in CH$_3$CN solution.

Table 3
Absorption and emission maxima of [Ag(DPEphos)(thione)$_2$]NO$_3$ complexes at room temperature.

Compound	λ_{max}[a] (nm)	λ_{em}[b] (nm)
[Ag(DPEphos)(py2SH)$_2$], **1**	287, 367	470, 420
[Ag(DPEphos)(pymtH)$_2$]NO$_3$, **2**	288, 374	483, 466
[Ag(DPEphos)(dmpymtH)$_2$]NO$_3$, **3**	283, 358	530, 410
[Ag(DPEphos)(thpymtH)$_2$]NO$_3$, **4**	286	390, 442
[Ag(DPEphos)(imtH)$_2$]NO$_3$, **5**	266	400, 438

[a] Solution in CH$_3$CN.
[b] Solid state (first entry), 10^{-5} M solution in CH$_3$CN (second entry).

significant shifting towards lower energies, in comparison with [Ag(DPEphos)$_2$]NO$_3$. This result may be considered as evidence for participation of S → Ag charge transfer in the emissive excited state [19]. On the other hand, compounds **4** and **5** show emission maxima which are further blue-shifted, in comparison with [Ag(DPEphos)$_2$]NO$_3$. Although these variations of the emission bands seem to be associated with the electronic characteristics of the thione ligands, nothing certain can be said before more detailed investigations on an extended dataset of related complexes have been carried out.

4. Conclusions

In this paper we describe the synthesis of five novel mixed-ligand silver nitrate complexes, bearing the bidentate bis[2-(diphenylphosphano)phenyl]ether and heterocyclic thiones as ligands. The new complexes are easily formed by the addition of the thione ligand to the AgNO$_3$–diphosphane adduct in dry acetonitrile. X-ray structural analysis of the pyridine-2-thione derivative reveals a slightly distorted tetrahedral geometry around the silver(I) metal center which is surrounded by the P atoms of the bidentate DPEphos and the two S-donor atoms of the py2SH ligands. The S-coordination mode of all the thiones used could be verified by the appearance of the four characteristic 'thioamide bands' in the recorded IR spectra of their respective complexes. The new compounds exhibit in the solid state and in solution at room temperature strong luminescence, with the excited-state responsible for the emission presumably having a metal perturbed IL character. Furthermore, there is strong evidence for a participation of S → Ag charge transfer in the emissive excited state, the extend of which could be associated with the electronic characteristics of the thione ligand.

Appendix A. Supplementary data

CCDC 842710 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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