

Supporting Information

Mechanochromism of Ag^I complexes with *i*PrNHC(S)NHP(S)(OiPr)₂

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Experimental Section

Physical measurements

Infrared spectra (Nujol) were recorded with a Thermo Nicolet 380 FT-IR spectrometer in the range 400–4000 cm⁻¹. NMR spectra (CDCl₃) were obtained on a Bruker Avance 300 MHz spectrometers at 25 °C. Fluorescence measurements were carried out on a SPEX FluoroMax-4 spectrofluorometer at room temperature. Electronic spectra of absorption in 10⁻⁴ M solution of CH₂Cl₂ were measured on a Lambda-35 spectrometer in the range 200–1000 nm. Electrospray ionization mass spectra were measured with a Finnigan MAT 95-XP mass spectrometer on a 10⁻⁶ M solution in CH₃OH. The speed of sample submission was 2 μL/min. The ionization energy was 4.5 kV. The capillary temperature was 200 °C. Ball-milling was performed using steel balls in a SPEX SamplePrep 8000M Mixer/Mill. Elemental analysis was performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments.

Synthesis of *i*PrNHC(S)NHP(S)(OiPr)₂ (**HL**)

A solution of *i*PrNH₂ (1.180 g, 20 mmol) in anhydrous CH₂Cl₂ (15 mL) was treated under vigorous stirring with a solution of (*i*PrO)₂P(S)NCS (5.019 g, 21 mmol) in the same solvent, and the mixture was stirred for 1 h. The solvent was then removed in vacuum. The residue was recrystallized from a CH₂Cl₂/*n*-hexane mixture (1:5, v/v).

Colorless crystals. Yield 5.789 g (97%). IR ν (cm⁻¹): 640 (P=S), 964 (POC), 1543 (S=C–N), 3090, 3382 (NH). ¹H NMR δ (ppm): 1.26 (d, ³J_{H,H} = 6.6 Hz, 6H, CH₃, *i*PrN), 1.33 (d, ³J_{H,H} = 6.2 Hz, 6H, CH₃, *i*PrO), 1.35 (d, ³J_{H,H} = 6.2 Hz, 6H, CH₃, *i*PrO), 4.47 (d. sept, ³J_{HNCH} = 8.0 Hz, ³J_{H,H} = 6.5 Hz, 1H, NCH), 4.79 (d. sept, ³J_{POCH} = 10.6 Hz, ³J_{H,H} = 6.2 Hz, 2H, OCH), 6.86 (br. s, 1H, NHP), 7.64 (br. s, 1H, alkylNH); ³¹P{¹H} NMR δ (ppm): 52.8. Anal. Calc. for C₁₀H₂₃N₂O₂PS₂ (298.40): C 40.25, H 7.77, N 9.39. Found: C 40.31, H 7.79, N 9.34%.

Synthesis of [*i*Ag₃(*i*PrNHC(S)NP(S)(OiPr)₂-S,S')₃]₂ (**[Ag₃L₃]₂**) and [*i*Ag₃(*i*PrNHC(S)NP(S)(OiPr)₂-S,S')₃]₃ (**[Ag₃L₃]₃**)

A suspension of **HL** (0.895 g, 3 mmol) in aqueous methanol (10 mL) was mixed with a methanol solution (10 mL) of KOH (0.185 g, 3.3 mmol). The resulting mixture was added dropwise to a suspension of AgPF₆ (0.758 g, 3 mmol) in aqueous methanol (10 mL). The mixture was stirred at room temperature for 5 h and. The resulting complex were extracted by CH₂Cl₂, and dried over anhydrous MgSO₄. The solvent was then removed in vacuum. The residue was recrystallized from a CH₂Cl₂/*n*-hexane mixture (1:3, v/v).

[Ag₃L₃]₂: Colourless crystals. Yield 1.094 g (90%). IR ν (cm⁻¹): 598 (P=S), 961, 973 (POC), 1504 (SCN), 3356 (NH). ¹H NMR δ (ppm): 1.17 (d, ³J_{H,H} = 6.4 Hz, 36H, CH₃, *i*PrN), 1.36 (d, ³J_{H,H} = 6.2 Hz, 72H, CH₃, *i*PrO), 3.98 (d. sept, ³J_{HNCH} = 7.1 Hz, ³J_{H,H} = 6.5

Hz, 6H, NCH), 4.76 (d sept, $^3J_{\text{POCH}} = 10.6$ Hz, $^3J_{\text{H,H}} = 6.1$ Hz, 12H, OCH), 6.39 (d, $^4J_{\text{PNCNH}} = 7.1$ Hz, 2H, alkylNH), 6.51 (d, $^4J_{\text{PNCNH}} = 6.7$ Hz, 4H, alkylNH); ^{13}C δ (ppm): 21.97 (s, CH₃, *i*PrN), 23.82 (d, $^3J_{\text{POCC}} = 3.4$ Hz, CH₃, *i*PrO), 45.69 (s, NCH), 72.54 (d, $^2J_{\text{POC}} = 8.0$ Hz, OCH), 169.24 (s, CS), 171.06 (s, CS); $^{31}\text{P}\{^1\text{H}\}$ NMR δ (ppm): 53.5 (s, 2P, NPS), 54.2 (br. s, 4P, NPS). ES-MS positive ion, *m/z* (%): 513.8 (96) [Ag₂L]⁺, 917.5 (84) [Ag₃L₂]⁺, 1216.8 (71) [Ag₃L₃ + H]⁺, 1255.2 (100) [Ag₃L₃ + K]⁺, 1323.1 (74) [Ag₄L₃]⁺, 1728.4 (62) [Ag₅L₄]⁺, 2133.6 (38) [Ag₆L₅]⁺, 2539.2 (17) [Ag₇L₆]⁺, 2945.2 (11) [Ag₈L₇]⁺; ES-MS negative ion, *m/z* (%): 297.7 (100) [L]⁻, 702.6 (72) [AgL₂]⁻, 1107.2 (62) [Ag₂L₃]⁻, 1512.8 (36) [Ag₃L₄]⁻, 1917.6 (52) [Ag₄L₅]⁻, 2322.7 (27) [Ag₅L₆]⁻, 2727.4 (9) [Ag₆L₇]⁻. *Anal. Calc.* for C₁₀H₂₂AgN₂O₂PS₂ (405.26): C 29.64, H 5.47, N 6.91. Found: C 29.56, H 5.41, N 6.96%.

[Ag₃L₃]: The white powder obtained after grinding of [(Ag₃L₃)₂] in a ceramic mortar. IR ν (cm⁻¹): 600 (P=S), 963, 972 (POC), 1506 (SCN), 3353 (NH). ^1H NMR δ (ppm): 1.15 (d, $^3J_{\text{H,H}} = 6.3$ Hz, 18H, CH₃, *i*PrN), 1.37 (d, $^3J_{\text{H,H}} = 6.1$ Hz, 36H, CH₃, *i*PrO), 3.99 (d sept, $^3J_{\text{HNCH}} = 7.1$ Hz, $^3J_{\text{H,H}} = 6.4$ Hz, 3H, NCH), 4.75 (d sept, $^3J_{\text{POCH}} = 10.6$ Hz, $^3J_{\text{H,H}} = 6.1$ Hz, H, OCH), 6.50 (s, 3H, alkylNH); ^{13}C δ (ppm): 22.01 (s, CH₃, *i*PrN), 23.84 (d, $^3J_{\text{POCC}} = 3.4$ Hz, CH₃, *i*PrO), 45.76 (s, NCH), 72.48 (d, $^2J_{\text{POC}} = 8.1$ Hz, OCH), 170.18 (s, CS); $^{31}\text{P}\{^1\text{H}\}$ NMR δ (ppm): 53.3 (s, NPS). ES-MS positive ion, *m/z* (%): 513.2 (70) [Ag₂L]⁺, 917.9 (100) [Ag₃L₂]⁺, 1216.4 (28) [Ag₃L₃ + H]⁺, 1255.7 (92) [Ag₃L₃ + K]⁺, 1323.5 (29) [Ag₄L₃]⁺; ES-MS negative ion, *m/z* (%): 297.9 (100) [L]⁻, 702.3 (38) [AgL₂]⁻, 1107.6 (42) [Ag₂L₃]⁻. *Anal. Calc.* for C₁₀H₂₂AgN₂O₂PS₂ (405.26): C 29.64, H 5.47, N 6.91. Found: C 29.58, H 5.42, N 6.95%.

*Mechanically induced solid-state synthesis of [Ag₃(*i*PrNHC(S)NP(S)(*Oi*Pr)₂-S,S')₃] (Ag₃L₃)*

The potassium salt **KL** (1.682 g, 5 mmol), which was obtained similar as described previously,¹ and AgPF₆ (1.264 g, 5 mmol) were ball-milled for eight hours. Then the powder was treated with CH₂Cl₂ (30 mL) for five minutes and filtered. The solvent was then removed in vacuum. The resulting product was analyzed by elemental analysis, IR and NMR spectroscopy. The obtained data testifies to the formation of the complex [Ag₃L₃] with the isolated yield 1.702 g (84%). The recrystallization of the powder complex [Ag₃L₃] from a CH₂Cl₂/*n*-hexane mixture (1:3, v/v) gives the X-ray suitable crystals of the complex [(Ag₃L₃)₂].

Crystal structure determination and refinement

The X-ray diffraction data for the crystal of [(Ag₃L₃)₂] were collected on a STOE IPDS-II diffractometer. The images were indexed, integrated and scaled using the X-Area package.² Data were corrected for absorption using the PLATON program.³ The structures were solved by direct methods using the SHELXS⁴ program and refined first isotropically and then anisotropically using SHELXL97.⁴ Hydrogen atoms were revealed from $\Delta\rho$ maps and refined using a riding model. All figures were generated using the program Mercury.⁵

CCDC 804264 contains the supplementary crystallographic. 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.

References

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Table S1. Crystal data, data collection and refinement details for $[(\text{Ag}_3\text{L}_3)_2]^a$

Empirical formula	$\text{C}_{60}\text{H}_{132}\text{Ag}_6\text{N}_{12}\text{O}_{12}\text{P}_6\text{S}_{12}$
Formula weight	2431.54
Temperature (K)	173(2)
Crystal system	triclinic
Space group	$P \bar{1}$
a (Å)	13.5494(2)
b (Å)	14.3050(2)
c (Å)	15.1930(2)
α (°)	109.1326(8)
β (°)	90.8079(8)
γ (°)	110.3766(7)
V (Å ³)	2580.54(6)
Z	1
D_{calc} (Mg m ⁻³)	1.565
μ (mm ⁻¹)	1.504
$F(000)$	1236
Recording range, θ_{max} (°)	2.64–26.37
Number of recorded reflections	39389
Number of recorded independent reflections	10241 ($R_{\text{int}} = 0.0389$)
R indices (all data)	$R_1 = 0.0641$, $wR_2 = 0.0869$

^a Measurements were made using Mo-K α with $\lambda = 0.71073$ (Å).

Table S2. Selected bond lengths (Å) and bond angles (°) for $[(\text{Ag}_3\text{L}_3)_2]^a$

<i>Bond lengths</i>					
Ag(1)···Ag(1A)	3.8262(5)	Ag(1B)–S(1B)	2.5079(10)	P(1B)–S(1B)	1.9726(16)
Ag(1)···Ag(1B)	3.9437(6)	Ag(1B)–S(2B)	2.5569(11)	S(2)–C(1)	1.776(4)
Ag(1A)···Ag(1B)	4.1709(5)	Ag(1B)–S(2)#1	2.6877(10)	S(2B)–C(1B)	1.746(4)
Ag(1)···Ag(1A)#1	4.7959(6)	S(2)–Ag(1A)	2.4382(10)	S(2A)–C(1A)	1.758(4)
Ag(1)···Ag(1B)#1	4.1153(4)	S(2A)–Ag(1B)	2.4889(10)	N(1)–C(1)	1.300(5)
Ag(1A)···Ag(1B)#1	4.3877(5)	P(1)–N(1)	1.603(3)	N(1A)–C(1A)	1.306(5)
Ag(1)–S(2B)	2.4210(10)	P(1A)–N(1A)	1.622(4)	N(1B)–C(1B)	1.323(5)
Ag(1)–S(2)	2.4665(11)	P(1B)–N(1B)	1.601(3)	C(1)–N(2)	1.333(5)
Ag(1)–S(1)	2.5251(12)	P(1)–S(1)	1.9810(16)	N(2A)–C(1A)	1.333(5)
Ag(1A)–S(1A)	2.4580(13)	P(1A)–S(1A)	1.992(2)	N(2B)–C(1B)	1.337(5)
Ag(1A)–S(2A)	2.5112(10)				
<i>Bond angles</i>					
S(2)–Ag(1)–S(1)	106.18(3)	Ag(1B)–S(2A)–Ag(1A)	113.05(4)	N(1A)–P(1A)–S(1A)	115.4(2)
S(2)–Ag(1A)–S(1A)	138.19(4)	Ag(1)–S(2)–Ag(1B)#1	105.88(3)	N(1B)–P(1B)–S(1B)	118.49(14)
S(2)–Ag(1A)–S(2A)	114.92(3)	Ag(1A)–S(2)–Ag(1B)#1	117.65(4)	C(1)–N(1)–P(1)	130.0(3)
S(2B)–Ag(1)–S(1)	125.03(4)	P(1)–S(1)–Ag(1)	89.15(5)	C(1A)–N(1A)–P(1A)	130.4(3)
S(2B)–Ag(1)–S(2)	127.11(4)	P(1A)–S(1A)–Ag(1A)	92.73(6)	C(1B)–N(1B)–P(1B)	130.2(3)
S(1A)–Ag(1A)–S(2A)	106.89(4)	P(1B)–S(1B)–Ag(1B)	95.92(5)	N(1)–C(1)–N(2)	119.9(3)
S(1B)–Ag(1B)–S(2B)	103.37(4)	C(1)–S(2)–Ag(1)	106.55(14)	N(1A)–C(1A)–N(2A)	118.0(4)
S(2A)–Ag(1B)–S(1B)	122.72(3)	C(1)–S(2)–Ag(1A)	106.15(12)	N(1B)–C(1B)–N(2B)	117.2(4)
S(2A)–Ag(1B)–S(2B)	125.75(3)	C(1)–S(2)–Ag(1B)#1	116.64(12)	N(1)–C(1)–S(2)	126.7(3)
S(1B)–Ag(1B)–S(2)#1	115.25(3)	C(1A)–S(2A)–Ag(1A)	101.15(13)	N(1A)–C(1A)–S(2A)	125.8(3)
S(2A)–Ag(1B)–S(2)#1	95.46(3)	C(1A)–S(2A)–Ag(1B)	109.62(15)	N(1B)–C(1B)–S(2B)	125.3(3)
S(2B)–Ag(1B)–S(2)#1	88.40(3)	C(1B)–S(2B)–Ag(1)	108.56(13)	N(2)–C(1)–S(2)	113.4(3)
Ag(1)–S(2B)–Ag(1B)	104.76(4)	C(1B)–S(2B)–Ag(1B)	102.53(14)	N(2A)–C(1A)–S(2A)	116.2(3)
Ag(1A)–S(2)–Ag(1)	102.54(3)	N(1)–P(1)–S(1)	117.28(13)	N(2B)–C(1B)–S(2B)	117.5(3)

^a Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y, -z + 1$.

Table S3. Hydrogen bond and hydrogen contact lengths (Å) and angles (°) for $[(\text{Ag}_3\text{L}_3)_2]^a$

D–H···A	$d(\text{D}–\text{H})$	$d(\text{H}···\text{A})$	$d(\text{D}···\text{A})$	$\angle(\text{DHA})$
N(2)–H(2)···O(2B)#1	0.89(4)	2.44(4)	3.236(5)	148(4)
N(2A)–H(2A)···S(1B)	0.899(10)	2.728(13)	3.620(4)	172(4)
N(2B)–H(2B)···S(1)	0.89(4)	2.77(4)	3.647(4)	170(4)
C(8)–H(8)···S(1)#2	0.98	2.99	3.95	166

^a Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y, -z + 1$; #2 $-x, -y, 1 - z$.

Table S4. UV-vis absorption and emission maxima for $[(\text{Ag}_3\text{L}_3)_2]$ and $[\text{Ag}_3\text{L}_3]^a$

Complex	λ_{abs} [nm] (ϵ [$\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$])	λ_{em} [nm]
$[(\text{Ag}_3\text{L}_3)_2]$	371 (8372)	573
$[\text{Ag}_3\text{L}_3]$	347 (4487)	469

^a The absorption spectrum of the potassium salt **KL** shows a weak absorption band at 298 nm ($\epsilon = 187 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

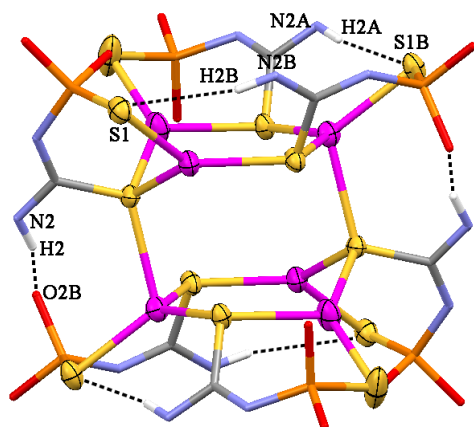


Figure S1. Hydrogen bonding in the crystal of the complex $[(\text{Ag}_3\text{L}_3)_2]$. Thermal ellipsoids at the 30% probability level (*i*Pr groups and H-atoms, not involved in hydrogen bonding, are omitted for clarity).