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Mechanochromism of Ag^I complexes with *i*PrNHC(S)NHP(S)(O*i*Pr)$_2$†

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Reaction of the potassium salt of *i*PrNHC(S)NHP(S)(O*i*Pr)$_2$ (HL) with AgPF$_6$ leads to the hexanuclear [{Ag$_3$(*i*PrNHC(S)-NP(S)(O*i*Pr)$_2$-*S*,*S′*)$_3$}$_2$] ([(Ag$_3$L$_3$)$_2$]) complex. The reversible conversion between yellow-emitting ([(Ag$_3$L$_3$)$_2$]) and blue-emitting ([Ag$_3$L$_3$]) materials on grinding and recrystallization was established. [Ag$_3$L$_3$] was also prepared by a mechanically induced solid-state reaction.

There are a number of Ag^I complexes with imidodiphosphinate ligands R$_2$P(X)NP(Y)R′$_2$ (**IDP**) (X, Y = O, S, Se, Te)[1] that are of great interest due to their use as catalysts[1a] and precursors for chalcogenide nanoparticles,[1h,i,k,l] and their electrochemical,[1e] and luminescent properties.[1n] In contrast to the **IDP** ligands, there is a lack of information about structures of Ag^I complexes containing *N*-thiophosphorylated thioureas and thioamides, RC(S)NHP(S)R′$_2$ (**NTT**), which are **IDP**'s asymmetrical analogues. The majority of Ag^I compounds with **NTT** are mixed-ligand complexes containing various phosphanes.[2] The molecular structure of only one polynuclear Ag^I complex, namely the cyclic tetramer [Ag$_4${PhC(S)NP(S)(O*i*Pr)$_2$}$_4$], has been reported.[3] We have also established that the reaction of Ag^I with the potassium salt of NH$_2$C(S)NHP(S)(O*i*Pr)$_2$ gives a new supramolecular complex [Ag(N═C–NP(S)(O*i*Pr)$_2$)]$_n$, that contains both tri- and tetracoordinated Ag^I.[4] Recently we have established that the reaction of the potassium salt **KL** with CuI or Cu(NO$_3$)$_2$ leads to the polynuclear complex [{Cu$_4$(*i*PrNHC(S)NP(S)(O*i*Pr)$_2$-*S*,*S′*)$_4$}$_2$], containing two tetrameric units [Cu$_4$L$_4$] attached to each other by eight Cu–S interactions.[5]

On the other hand it was established that some transition metal complexes might exhibit remarkable changes of their properties (*e.g.* luminescent properties) upon mechanical force.[6] However, it is rather difficult to find a reasonable explanation for these changes.

In this work, we describe the complete structural and spectroscopic characterization of a new hexanuclear Ag^I complex [{Ag$_3$(*i*PrNHC(S)NP(S)(O*i*Pr)$_2$-*S*,*S′*)$_3$}$_2$] ([(Ag$_3$L$_3$)$_2$]). Its luminescent properties reveal an intriguing emitting colour change upon mechanical grinding.

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The reaction of the potassium salt **KL** with AgPF$_6$ leads to the hexanuclear [(**Ag$_3$L$_3$)$_2$**] complex (Scheme 1, for detailed synthesis see the ESI†). Colourless crystals of [(**Ag$_3$L$_3$)$_2$**] were obtained by recrystallization from CH$_2$Cl$_2$/*n*-hexane (1 : 3, v/v).

Scheme 1
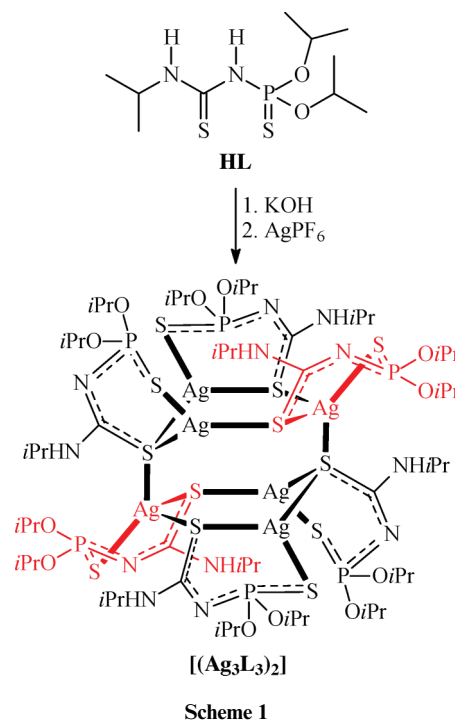
The IR spectrum of [(**Ag$_3$L$_3$)$_2$**] shows a weak band at 598 cm^{-1} assigned to the P═S groups. It is shifted to low frequencies relative to that in the spectrum of the parent ligand **HL** (640 cm^{-1}) due to the coordination with the metal cation.[7] The broad and strong band at 1504 cm^{-1} is assigned to the conjugated SCN group.[8] A unique band at 3356 cm^{-1} related to the alkyl NH group was also observed.

The ^{31}P{^{1}H} NMR spectrum of [(**Ag$_3$L$_3$)$_2$**] contains two singlet signals at 53.5 (narrow singlet) and 54.2 (broadened singlet) ppm with the integral intensities ratio of 2 : 4. The signals are in the region that is characteristic for deprotonated **NTT**.[7] We assume that the former signal corresponds to the phosphorus atoms of the deprotonated ligands **L**, which are coordinated to the bridging Ag^I cations (in red in Scheme 1). The ^{13}C NMR spectrum of [(**Ag$_3$L$_3$)$_2$**] contains a characteristic set of signals for the *i*PrN and *i*PrO carbons. Interestingly, there are two signals for the carbon

atoms of the C=S groups at 169.24 and 171.06 ppm. The ^{1}H NMR spectrum of [(**Ag₃L₃**)₂] also contains a set of signals for the *i*PrN and *i*PrO protons. It is noteworthy that the ^{1}H NMR spectrum of [(**Ag₃L₃**)₂] contains two signals for the NH protons, which are observed as doublets at 6.39 and 6.51 ppm with the integral intensities ratio of 2 : 4 and rather high $^4J_{PNCNH}$ (7.1 and 6.7 Hz, respectively) coupling constants. These constants are explained by the fact that the PNCNH chain in the complex [(**Ag₃L₃**)₂] meets the so-called *W*-criterion in a CDCl₃ solution.[9] Thus, according to the NMR spectroscopy data the complex [(**Ag₃L₃**)₂] contains two types of ligands at least in CDCl₃ solution (Scheme 1).

The ES mass spectra of the [(**Ag₃L₃**)₂] complex were measured in the positive and negative ion regime. In the mass spectrum of the positive ions the heaviest peak corresponds to the [Ag₈L₇]⁺ cation. Besides, there are intense peaks for the [Ag₂L]⁺, [Ag₃L₂]⁺, [Ag₄L₃]⁺, [Ag₅L₄]⁺, [Ag₆L₅]⁺ and [Ag₇L₆]⁺ ions. The two peaks [Ag₃L₃ + H]⁺ and [Ag₃L₃ + K]⁺, characteristic for the trinuclear molecular species, were also fixed. The latter peak is the most intense in the mass spectrum. The negative ES mass spectrum of [(**Ag₃L₃**)₂] contains peaks of the polynuclear anions [Ag₂L₃]⁻, [Ag₃L₄]⁻, [Ag₄L₅]⁻, [Ag₅L₆]⁻, [Ag₆L₇]⁻. The most intense peaks correspond to the ligand anion [L]⁻ and the mononuclear species [AgL₂]⁻.

The crystal structure of the complex [(**Ag₃L₃**)₂] was determined by single crystal X-ray diffraction (see Table S1 in the ESI†). The complex crystallizes in the triclinic space group $P\bar{1}$ (Z = 1). Each metal cation is bound to the deprotonated thiophosphoryl thiourea through the sulfur atoms of the C=S and P=S groups forming a six-membered heterometallocyclic chelate [AgL] (Fig. 1). The phosphorus atom is out of plane of the pseudo boat conformation. The C=S bonds are longer (see Table S2 in the ESI†) than those found in other thioureas and thioamides.[7] The standard reference values for the P=S double and P–S single bonds are 1.92 and 2.10 Å, respectively.[10] Partial double bonds occur between the P and S (see Table S2 in the ESI†). All C–N–P angles fall within the range from 130.0(3)° to 130.4(3)°. Six

Fig. 1 Thermal ellipsoid (30%) plot of [(**Ag₃L₃**)₂]. H-atoms have been omitted for clarity.

[AgL] moieties associate to form a hexamer [Ag₆L₆], which can also described as two trimeric units [Ag₃L₃] attached to each other by two Ag–S interactions (Fig. 1). The six-membered chelate rings are linked by the thiocarbonyl sulfur atoms resulting in a six-membered Ag₃S₃ ring, which contains the almost planar Ag1–S2B–Ag1B–S2A–Ag1A fragment with the S2 sulfur atom being deviated from this plane (Fig. 1). Contrary to our expectations, the hexameric unit is also formed by Ag–S interactions through the thiocarbonyl sulfur atoms, while the thiophosphoryl sulfur atoms in each ligand moiety still form only one Ag–S bond (Fig. 1). Due to this type of coordination the structure of the [(**Ag₃L₃**)₂] complex contains two types of silver and thiocarbonyl sulfur atoms. There are four silver atoms (Ag1 and Ag1A) in a planar trigonal S₃ environment (Fig. 1) with the sum of the S–Ag1–S and S–Ag1A–S angles being 358.32° and 360°, respectively (see Table S2 in the ESI†). The S–Ag1B–S angle range is from 88.40(3)° to 125.75(3)° (see Table S2 in the ESI†). Thus, these two Ag^I atoms have a distorted tetrahedral environment (Fig. 1). The S2A and S2B sulfur atoms are μ₂-coordinated to two Ag^I atoms, while the S2 atoms exhibit μ₃-coordination modes towards three Ag^I atoms with the formation of two bridging Ag1B–S2#1 bonds (Fig. 1). These bridging bonds are the longest among the Ag–S distances in the structure of the [(**Ag₃L₃**)₂] complex (see Table S2 in the ESI†). All Ag···Ag separations (see Table S2 in the ESI†) are longer than twice the van der Waals radius of this metal (3.440 Å),[11] which indicates that a significant interaction does not occur between the silver atoms. The complex [(**Ag₃L₃**)₂] contains in the crystal six intramolecular hydrogen bonds (see Fig. S1 and Table S3 in the ESI†). There are four *i*Pr–NH···S=P H-bonds between neighbouring ligands in each trinuclear [Ag₃L₃] units of the molecule. The other two hydrogen bonds *i*Pr–NH···O–P are formed between the bridging ligand of one trinuclear [Ag₃L₃] unit and the ligand of another trinuclear [Ag₃L₃] unit corresponding to the same molecule. Furthermore, the molecules of [(**Ag₃L₃**)₂] in the crystal are bound through four intermolecular NC–H···S=P contacts forming polymeric chains (see Table S3 in the ESI†).

The absorption spectrum of [(**Ag₃L₃**)₂] was studied in CH₂Cl₂ solution, whereas the luminescent properties were investigated both in the solid state and in CH₂Cl₂ at room temperature (see Table S4 in the ESI†). A strong absorption band at 371 nm ($ε$ = 8372 dm³ mol⁻¹ cm⁻¹) is observed in the spectrum of [(**Ag₃L₃**)₂]. Absorption bands for the free and protonated **NTT** ligands are rather high in energy ($λ_{max}^{abs}$ <250 nm) and were assigned to intraligand transitions.[2c,12] For better comparison with the [(**Ag₃L₃**)₂] complex in which the ligands are deprotonated, we recorded the spectrum of the corresponding potassium salt **KL**. The absorption spectrum of **KL** contains a weak band at 298 nm ($ε$ = 187 dm³ mol⁻¹ cm⁻¹),[5] that can be attributed to the ligand–ligand transition in the deprotonated form **L**. The absorption band of the [(**Ag₃L₃**)₂] complex is thus assigned to ligand-to-cluster or cluster-centred charge transfer transitions.

The colourless crystals of [(**Ag₃L₃**)₂] show emission in the solid state at 573 nm upon irradiation at 364 nm (note that neither **HL** nor **KL** show any emission in the solid state) (see Table S4 in the ESI†). The emission of [(**Ag₃L₃**)₂] might evolve from ligand-to-metal charge transfer transitions, mixed with ligand-to-cluster and cluster-centred charge transfer transitions, which have been concluded for the emissions of Cu^I and Ag^I compounds with similar **NTT** ligands.[2c,12d–12f] However the [(**Ag₃L₃**)₂] complex shows
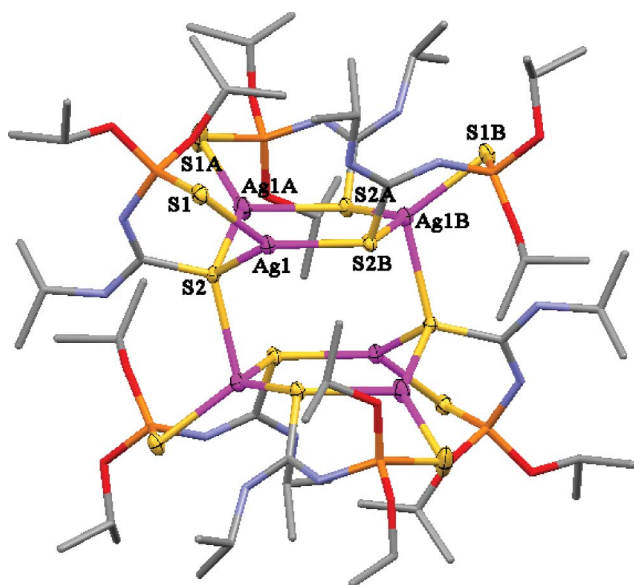
no emission in CH_2Cl_2, which is obviously due to quenching since its polynuclear structure is preserved in solution. At the moment, it is difficult to establish the exact origin for the emission displayed by Ag^I polynuclear complexes with **NTT** ligands because of the absence of in-depth photophysical studies. However, the origin of luminescence for d^{10} metal clusters is obviously dependent on the metal core features observed in the solid state and in solution.[13]

When the yellow-emitting crystals of $[(Ag_3L_3)_2]$ were ground in a ceramic mortar, the resulting white powder was found to emit blue luminescence at 469 nm (see Table S4 in the ESI†). The elemental analysis and IR spectra (mechanical grinding in Nujol) of both crystals and powder gave the same data (see the Experimental Section in the ESI†) suggesting that the observed phenomenon is not caused by adsorption or removal of solvent.

The $^{31}P\{^1H\}$ NMR spectrum of the white powder contains one singlet signal at 53.3 ppm. Since this signal is also in the region that is characteristic for deprotonated **NTT**,[7] we can conclude the presence of deprotonated ligands **L** in the structure of the white powder. ^{13}C and ^1H NMR spectra of the white powder are similar to those of crystals of $[(Ag_3L_3)_2]$. The main difference involves the peaks of the C=S carbon atoms and the NH protons, which are shown as one peak in the corresponding spectra of the white powder. Furthermore, the signal of the NH protons is shown as a singlet. This might be the evidence for the fact that the PNCNH chain in the white powder does not meet the W-criterion in a $CDCl_3$ solution.[9]

In the mass spectrum of the positive ions of the white powder the heaviest peak corresponds to the $[Ag_4L_3]^+$ cation. There are also intense peaks for the $[Ag_2L]^+$ and $[Ag_3L_2]^+$ ions. The two peaks $[Ag_3L_3 + H]^+$ and $[Ag_3L_3 + K]^+$, characteristic for the trinuclear molecular species, were also observed. The negative ES mass spectrum contains peaks for the mono- $[AgL_2]^-$ and dinuclear $[Ag_2L_3]^-$ anions. The most intense peak also corresponds to the ligand anion $[L]^-$.

The absorption spectrum of the white powder in CH_2Cl_2 contains an absorption band at 347 nm ($\varepsilon = 4487$ dm^3 mol^{-1} cm^{-1}). This band is markedly blue-shifted from the band in the spectrum of $[(Ag_3L_3)_2]$ and shows a much lower extinction coefficient. The white powder also shows emission in the solid state at 469 nm upon irradiation at 342 nm.

Comparison of the elemental analysis, IR, NMR, mass spectrometry and photophysical data of the white powder and $[(Ag_3L_3)_2]$ is the evidence for the same composition and the structural similarity of these compounds. However, we assume the white powder has less nuclearity compared to the hexanuclear complex $[(Ag_3L_3)_2]$ and we suggest a $[Ag_3L_3]$ formulation. Numerous attempts to crystallize this trinuclear complex failed or led to the formation of the hexanuclear complex $[(Ag_3L_3)_2]$. The obtained data show the reversible conversion from the yellow-emitting crystals of $[(Ag_3L_3)_2]$ to the blue-emitting powder of $[Ag_3L_3]$ on mechanical grinding and recrystallization. Furthermore, attempts to repeat these yellow-to-blue emission cycles were successful at least eight times.

The complex $[Ag_3L_3]$ was also prepared by a mechanically induced solid-state reaction (for detailed synthesis see the ESI†). The solid potassium salt **KL** and $AgPF_6$ were ball-milled in a hardened-steel vial with steel balls for eight hours. The resulting product was analyzed by elemental analysis, IR and NMR spectroscopy. The photophysical properties were also investigated.

The obtained data unequivocally testifies to the formation of the complex $[Ag_3L_3]$.

In summary, the reaction of $AgPF_6$ with the potassium salt of iPrNHC(S)NHP(S)(OiPr)$_2$ has allowed us to obtain a new polynuclear Ag^I complex $[(Ag_3L_3)_2]$, which shows reversible conversion between the yellow-emitting complex $[(Ag_3L_3)_2]$ and the blue-emitting complex $[Ag_3L_3]$ on grinding and recrystallization. The observed mechanochromism results from the reversible change of nuclearity. Furthermore, the mechanically induced solid-state formation of the d-metal complex of the **NTT** ligands has been observed for the first time. It was established that the solid-state reaction of **KL** and $AgPF_6$ leads to the formation of the trinuclear complex $[Ag_3L_3]$ with an isolated yield of 84%. The spectroscopic and photophysical characteristics of the complex $[Ag_3L_3]$ are the same regardless of the synthesis conditions.

Acknowledgements

Notes and references

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