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# Solid State $^{31}\text{P}$ and $^{109}\text{Ag}$ CP/MAS NMR as a powerful tool for studying of Silver(I) Complexes with N-Thiophosphorylated Thiourea and Thioamide ligands

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KEYWORDS Solid state NMR,  $^{31}\text{P}$  and  $^{109}\text{Ag}$  NMR, N-Thiophosphorylthiourea, Silver(I) complexes, Polynuclear complexes.

ABSTRACT. A family of three- and four-coordinated silver(I) complexes of formulas  $[\text{Ag}(\text{PPh}_3)_2\text{L}]$ ,  $[\text{Ag}(\text{PPh}_3)\text{L}]$  and  $[\text{AgL}]_n$  with N-thiophosphorylated thiourea and thioamide ligands of general formula  $\text{RC}(\text{S})\text{NHP}(\text{S})(\text{OPri})_2$  [ $\text{R} = \text{Ph}, \text{PhNH}, i\text{PrNH}, t\text{BuNH}, \text{NH}_2$ ] have been studied by solid-state  $^{109}\text{Ag}$  and  $^{31}\text{P}$  CPMAS NMR spectroscopy.  $^{109}\text{Ag}$  NMR spectra have provided valuable structural information about Ag coordination, which is in good accordance with the available crystal structure data. The data presented in this work represent a significant addition to the available  $^{109}\text{Ag}$  chemical shifts and chemical shifts anisotropies. The silver chemical shift ranges for different P,S-environments and coordination state were discussed in detail. The  $^1J(^{31}\text{P}-^{107/109}\text{Ag})$  and  $^2J(^{31}\text{P}-^{31}\text{P})$  values were determined and analyzed.

## INTRODUCTION

In spite of the fact that there are many new developments and frequent applications of different silver containing materials, the silver solid-state NMR spectroscopy is rarely used and rarely mentioned. To the best of our knowledge, the more recent review we found was published over fifteen years ago.<sup>[1, 2]</sup> There are three major reasons for this rareness: low gyromagnetic ratios ( $\gamma$ ), low receptivity, and the rather large longitudinal relaxation time. Low gyromagnetic ratios leads to the acoustic probe ringing which obliterates FIDs. Low receptivity and the rather large longitudinal relaxation time make the acquisition of silver NMR spectra very challenging. Let us additionally note other experimental difficulties that we encountered in the realization of this

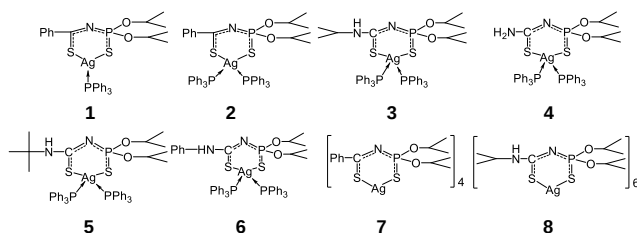
work and which were not extensively discussed in previous in works: a wide and unknown for different environments the silver chemical shift range, which associated in solid state with high values of chemical shift anisotropy parameter.

Currently, copper(I) complexes attract a special interest as promising emitting materials for OLED devices, solar cells, photocatalysts and bioimaging agents.<sup>[3]</sup> Only a limited example of silver(I) complexes exhibit phosphorescence at room temperature.<sup>[4]</sup> Unlike to the related Cu (I) complexes, the energetically lower d-orbitals of silver(I) lead to a larger band gap and, consequently, cause a change of spectral band position in the absorption and emission spectrum. Contrastingly, to Cu (I), the higher oxidation potential of Ag (I) due to the greater stabilization of d-electrons leads to the diminution the probability of electronic transitions in Metal-to-Ligand Charge Transfer. Therefore, Ag (I) luminophores exhibit less a delayed fluorescence than their Cu (I) analogs.<sup>[5]</sup>

Herein, we report upon the solid-state  $^{31}\text{P}$  and  $^{109}\text{Ag}$  NMR characterization of a series of metallocomplexes, in which the silver has the coordination number of three or four and surrounded by sulfur and phosphorus atoms. N-(Thio)phosphorylated derivatives of the thioamides and thioureas of general formula  $\text{RC}(\text{S})\text{NHP}(\text{X})(\text{OR}')_2$  (**TPT**,  $\text{X} = \text{O}, \text{S}$ ) attract attention due to their versatile complexing properties<sup>[6]</sup> and easy structure modification by changing the nature of X donor site and structure of the R-moiety.<sup>[7]</sup> Changing of these key sites result in dramatically changes of the coordination properties of the **TPT** ligands. Besides the obvious factors concerned the nature of the ligand donor atom X, the structure of such complexes can be determined by: 1) electronic effects of the substituents, even quite far from the coordination core, 2) influence of the intramolecular interactions in the ligand structure, e. g.

hydrogen bonds, 3) steric factors. Moreover, the influence of these secondary factors can have crucial importance.

The structural formulas of eight studied silver(I) complexes of formulas  $[\text{Ag}(\text{PPh}_3)_2\text{L}]$ ,  $[\text{AgL}]_n$  and  $[\text{Ag}(\text{PPh}_3)\text{L}]$  with **TPT** ligands of general formula  $\text{RC}(\text{S})\text{NHP}(\text{S})(\text{OPri})_2$  [ $\text{R} = \text{Ph}$   $\text{L}^{\text{a}}$ ,  $i\text{PrNH}$   $\text{L}^{\text{b}}$ ,  $\text{NH}_2$   $\text{L}^{\text{c}}$ ,  $t\text{BuNH}$   $\text{L}^{\text{d}}$ ,  $\text{PhNH}$   $\text{L}^{\text{e}}$ ] are presented in Scheme 1. The synthesis are described in previously reported studies.<sup>[8-10]</sup>



SCHEME 1. The structural formulas of the studied silver complexes.

Numerous silver complexes in solution undergo a rapid ligand exchange on the NMR time-scale.<sup>[1]</sup> This phenomenon hides useful information about spin–spin couplings and gives average chemical shifts. The solid-state NMR technique has proved to be a significant tool for the investigation of local structure around a silver core, without limitations due to a dynamics. Magic angle spinning (MAS) NMR on metal nuclei is very useful because it gives direct information about central atom of a complex: coordination numbers, coordination environments, or the distortion of coordination environments.

## EXPERIMENTAL

$^{31}\text{P}$  and  $^{109}\text{Ag}$  solid-state MAS NMR were carried out on a Bruker Avance 400 (9.4 T) spectrometer using a 4 mm and 7 mm probe-heads respectively. The  $^1\text{H}$ - $^{31}\text{P}$  cross-polarization (CP) MAS NMR spectra were recorded at a spinning frequency of 14 kHz using a ramped cross-

polarization<sup>[11]</sup> with a contact time of 1 ms and a recycle delay of 2 s. <sup>1</sup>H decoupling was achieved using the SPINAL-64 sequence<sup>[12]</sup> with a <sup>1</sup>H nutation frequency of about 60 kHz. Quantitative MAS spectra were acquired using a single pulse of 0.5  $\mu$ s duration ( $\pi/12$ ) and a recycle delay of 1 s. Chemical shift is referred to 85 % H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) solution. For the compounds **4** and **6**, additionally, <sup>31</sup>P MAS spectra were carry out on a Bruker Avance III 750 (17.6 T) using a 4 mm probe. <sup>109</sup>Ag magic angle spinning experiments were performed with sample spinning rates 3 kHz. Cross-polarization experiments used contact times of 20 ms and a recycle delay of 2 s, number of scans was between 10000 and 420000 depending on the signal-to-noise ratio required. <sup>1</sup>H decoupling was achieved using the SPINAL-64 sequence with a <sup>1</sup>H nutation frequency of about 60 kHz. The <sup>109</sup>Ag chemical shift of solid AgSO<sub>3</sub>CH<sub>3</sub> (87.2 ppm) was used as a reference.<sup>[13]</sup> For the compounds **1**, **7**, and **8**, additionally, the data were collected at rotor frequencies of 2.7 and 3.3 kHz. The different spinning speeds were used to distinguish spinning sidebands (ssb) from isotropic peaks. All MAS NMR spectra were modeled using the *Dmfit* program.<sup>[14]</sup>

## RESULTS

### <sup>31</sup>P solid state NMR.

The structures of the eight crystalline complexes were characterized by <sup>31</sup>P and <sup>109</sup>Ag solid-state MAS NMR spectroscopy. Modeling of NMR spectra using the *Dmfit* program has allowed to obtain chemical shifts, *J*-coupling constant values, and anisotropy parameters (Table 1 and 2). Crystal structures determined by single crystal X-Ray diffraction are known for some of these complexes namely for **1**,<sup>[15]</sup> **2**,<sup>[15]</sup> **3**,<sup>[16]</sup> **7**,<sup>[9]</sup> and **8**.<sup>[10, 17]</sup>

In the <sup>1</sup>H-<sup>31</sup>P CPMAS spectrum of **1** (Figure 1Sa), the resonance of the P atom of the thiophosphoryl group appears as a single peak. At the same time, the triphenylphosphine group

gives a doublet owing to the direct  $J$ -couplings with the both  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  isotopes. Due to relatively small isotope shift of the  $^{31}\text{P}$  signal and the close value of the coupling constants (the ratio  $J$ -couplings is proportional to the ratio they gyromagnetic ratios  $\gamma^{107}\text{Ag}/\gamma^{109}\text{Ag}=0.87$ ), the subspectra of the molecules with  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  nucleus demonstrate no splitting in the experimental conditions. The overall  $^1J(^{31}\text{P}-^{107,109}\text{Ag})$  values are observed in the most of our samples (the only exception is the complex **4**, see later.) and also in the previous studies.<sup>[18, 19]</sup>

The  $^1\text{H}$ - $^{31}\text{P}$  CPMAS spectra of **2**, **3**, and **5** show singlet signals for the thiophosphoryl group and two doublet of doublets for the inequivalent  $\text{PPh}_3$  phosphorus atoms, which are a result of  $^1J(^{31}\text{P}-^{107/109}\text{Ag})$  and  $^2J(^{31}\text{P}-^{31}\text{P})$  coupling (Figure 1S). The NMR measurements fit with the X-ray studies of the mononuclear complex **2**, containing three different P-sites. The X-ray data shows that the unit cell has two identical asymmetric units, which contain two molecules of **2** each.<sup>[15]</sup> The values of the  $^{31}\text{P}$  isotropic chemical shifts,  $^2J(^{31}\text{P}-^{31}\text{P})$ , and overall  $^1J(^{31}\text{P}-^{107/109}\text{Ag})$  coupling constants confirm a similarity of structure of three cores of complexes **2**, **3**, and **5** (Table 1). Crystal structure of the close analog of these compounds of formula  $[\text{Ag}(\text{HL}^a)(\text{PPh}_3)_2]\text{OTf}$  (**9**) was reported in 20. The complex **9** has the similar  $\text{AgP}_2\text{S}_2$  tetrahedral environment around the silver(I) cation. The neutral form of the ligand  $\text{HL}^a$  demonstrates the same  $S,S'$ -bidentate coordination mode and the similar geometry of the ligand moiety.

$^1\text{H}$ - $^{31}\text{P}$  CPMAS spectrum of complex **4** contains two independent sets of signals of the same intensity and similar splitting patterns (Figure 1). Each of the sets has one singlet for the thiophosphoryl group and two doublets of doublets for two independent  $\text{PPh}_3$  groups. To improve the resolution and to have unambiguous fit parameters, additionally, the compound **4** was measured at second magnetic high field 17.6 T (Figure 2S). Then, the both spectra were modeled using a single consistent set of parameters. These sets of signals could be assigned to

the two isomers in the asymmetric unit of the compound **4**. This crystal structure can be created due to the formation of the more dense crystal packing as well as different non-valent intermolecular interactions. It should be noted that such structural motif is well known in different organic and metalloorganic compounds, see for example, the review<sup>[21]</sup> or the recent work about the crystal structure of silver complex.<sup>[22]</sup> There is another possibility of explaining signal doubling what is the coexistence of two polymorphs in the sample, which is also a common occurrence. Unfortunately, there is no any X-Ray data for this compound up to now so we can't prove our assumption.

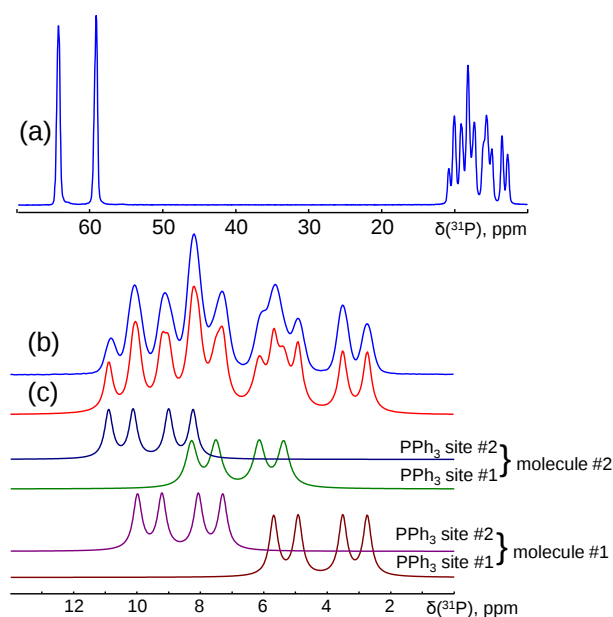


FIGURE 1. (a) Solid state  $^1\text{H}$ - $^{31}\text{P}$  CPMAS NMR spectrum recorded at 9.4 T of the complex **4**. Expansion of the (b) experimental and (c) simulated  $J$ -multiplet patterns of the  $\text{PPh}_3$  ligands.

Unlike in previous examples,  $^1\text{H}$ - $^{31}\text{P}$  CPMAS spectra recorded at two magnetic fields (9.4 T and 17.6 T) of **6** contain the signal of the phosphorus atom of the thiophosphoryl group and two more complex sets of signal for two different triphenylphosphine P sites (Figure 2). The each set represents two doublets of doublets owing to the couplings of the phosphorus atom to two

different isotopes of silver  $^1J(^{31}\text{P}-^{107}\text{Ag})$ ,  $^1J(^{31}\text{P}-^{109}\text{Ag})$  and between themselves  $^2J(^{31}\text{P}-^{31}\text{P})$ . Resulting multiplet was solved by *Dmfit* taking into account the natural abundances of the  $^{107}\text{Ag}$  (51.82 %) and  $^{109}\text{Ag}$  (48.18 %) isotopes.

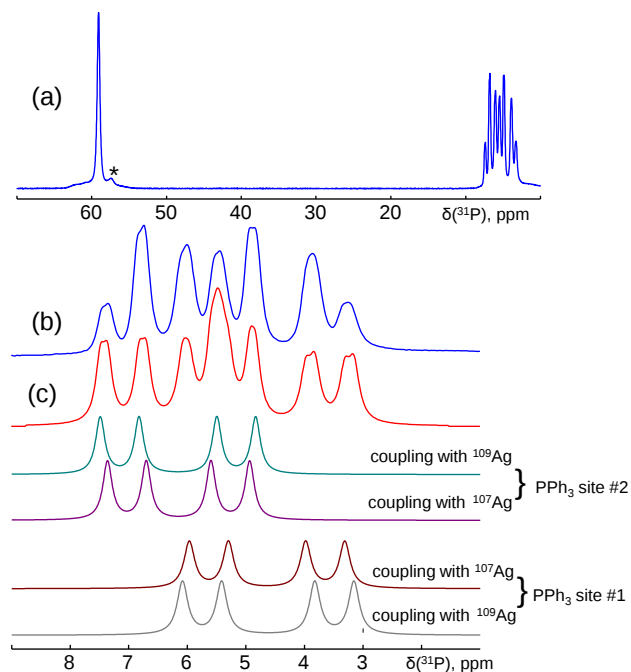


FIGURE 2. The solid state  $^1\text{H}$ - $^{31}\text{P}$  CPMAS NMR spectrum of the complex **6** (a). Expansion of the experimental (b) and simulated  $J$ -multiplet patterns (c) of the  $\text{PPh}_3$  ligands. \*-secondary phase.

The cyclic tetramer  $[\text{Ag}_4\text{L}^{\text{a}}_4]$  **7** in a crystal possesses  $S_4$ -symmetry, and all four phosphorus atoms are crystallographically equivalent.<sup>[9]</sup> The singlet signal is observed in the  $^1\text{H}$ - $^{31}\text{P}$  CPMAS spectra (Figure S1e). Therefore, our NMR observation is in exact agreement with the X-ray data. The another cyclic tetramer  $[\text{Ag}_4\text{L}_4]$  with  $\text{L} = \text{o-MeO}(\text{O})\text{CC}_6\text{H}_4\text{NHC}(\text{S})\text{NP}(\text{S})(\text{OPr-}i)_2$  has a similar core with  $S_4$ -symmetry.<sup>[23]</sup> It is interesting to note that the copper analog of **7** in crystal contains a similar cyclic tetramer of the same formula  $[\text{Cu}_4\text{L}^{\text{a}}_4]$  but with lower symmetry  $S_2$ .<sup>[24]</sup>

The  $^1\text{H}$ - $^{31}\text{P}$  CPMAS spectrum of polynuclear silver complex **8** is shown in Figure 3. The spectrum contains three resolved resonances with relative intensities in the ratio 1:1:1. The molecule of centrosymmetric hexanuclear complex  $[\text{Ag}_6\text{L}^b_6]$  **8** consists of two coaxial  $[\text{Ag}_3\text{L}^b_3]$  cycles interlinked by two Ag-S bonds. The aggregation is provided by the thiocarbonyl sulfur, all of the thiophosphoryl sulfur atoms in the structure form only one Ag-S bond. These two Ag-S-Ag-S-Ag-S cyclic moieties have an envelope conformation with the deviation of the four-coordinate S atoms from the main plane of the cycle. All three P-S moieties in each cycle are crystallographically inequivalent. Thus, the  $^1\text{H}$ - $^{31}\text{P}$  CPMAS spectrum clearly fits well with a crystal structure and the ratio corresponds to the three inequivalent P-S moieties per molecule.

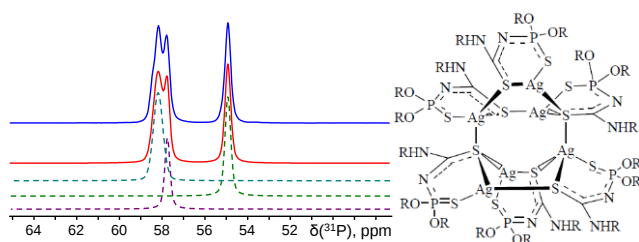


FIGURE 3. On the left,  $^1\text{H}$ - $^{31}\text{P}$  CPMAS NMR spectrum of complex **8** (blue) and reconstructed (red). Dashed lines display the decomposition of the theoretical spectrum in its individual components. On the right, the structural formula of **8**.

### $^{109}\text{Ag}$ solid state NMR.

The  $^1\text{H}$ - $^{109}\text{Ag}$  CPMAS NMR spectra for the obtained chelates (**1-6**) represents an expected multiplet patterns in total agreement with the obtained  $^1\text{H}$ - $^{31}\text{P}$  CPMAS data. There is doublet of doublets in the spectra of all  $[\text{Ag}(\text{PPh}_3)_2\text{L}]$  chelates (**2**, **3**, **4**, and **5**) due to two  $^1J(^{31}\text{P}-^{109}\text{Ag})$  with the two inequivalent  $\text{PPh}_3$  phosphorus units (Table 2 and Figure S3). The trigonal complex **1** shows one doublet with a significantly higher  $^1J$  value compared to the tetrahedral analogues. Unlike in previous experiments, this doublet has a several intense spinning sidebands due to the

large chemical shift anisotropy of AgS<sub>3</sub> site (Figure S4). The spectrum of **6** exhibits two set of doublet of doublets (Figure S3). All measured  $^1J(^{31}\text{P}-\text{Ag})$  values (329–380 Hz) are significantly lower in comparison with  $J$  values (643–733 Hz) reported for mixed carboxylate bis(diphenylphosphino)methane complexes with AgO<sub>2</sub>P and AgO<sub>3</sub>P coordination of the metal atom from solid state and solution  $^{31}\text{P}$  NMR experiments.<sup>[25]</sup> The closer data (203–330 Hz) were found for the complexes of silver(I) nitrate with 1,2-bis(di-*n*-pyridylphosphino)ethane (dnpype) with AgP<sub>4</sub> coordination core.<sup>[26]</sup>

As noted above, in phosphorus spectra the overall  $^1J(^{31}\text{P}-^{107,109}\text{Ag})$  values are observed in the most cases (Table 1). To compare the  $J$  coupling constants obtained from  $^{31}\text{P}$  and  $^{109}\text{Ag}$  spectra, the following calculations were made. The  $^1J(^{31}\text{P}-^{107/109}\text{Ag})$  coupling constants observables from  $^{31}\text{P}$  spectra can be present as  $^1J_{\text{over}} = ^1J(^{31}\text{P}-^{107}\text{Ag}) \times \text{Nat.ab.}^{107}\text{Ag} + ^1J(^{31}\text{P}-^{109}\text{Ag}) \times \text{Nat.ab.}^{109}\text{Ag}$ , where  $\text{Nat.ab.}^{107}\text{Ag}$  and  $\text{Nat.ab.}^{109}\text{Ag}$  are natural abundance for 107 and 109 isotopes, respectively. In consideration of  $^1J(^{31}\text{P}-^{107}\text{Ag}) = ^1J(^{31}\text{P}-^{109}\text{Ag}) \times \gamma^{107}\text{Ag} / \gamma^{109}\text{Ag}$ , where  $\gamma^{107}\text{Ag}$  and  $\gamma^{109}\text{Ag}$  are gyromagnetic ratios for 107 and 109 isotopes, respectively. We obtain  $^1J_{\text{over}} = ^1J(^{31}\text{P}-^{109}\text{Ag}) \times \gamma^{107}\text{Ag} / \gamma^{109}\text{Ag} \times \text{Nat.ab.}^{107}\text{Ag} + ^1J(^{31}\text{P}-^{109}\text{Ag}) \times \text{Nat.ab.}^{109}\text{Ag}$ . And finally by substituting the values of  $\text{Nat.ab.}^{107}\text{Ag} = 51.82\%$ ,  $\text{Nat.ab.}^{109}\text{Ag} = 48.18\%$  and  $\gamma^{107}\text{Ag} / \gamma^{109}\text{Ag} = 0.87$  in equation, we get  $^1J_{\text{over}} = 0.932634 \times ^1J(^{31}\text{P}-^{109}\text{Ag})$ . The values  $^1J(^{31}\text{P}-^{109}\text{Ag})$  were obtained directly from  $^{109}\text{Ag}$  NMR spectra (Table 2). The calculated values  $^1J_{\text{over}}$  are presented in the Table 1 and they are in a very good agreement with the values obtained from the fitting of the experimental  $^{31}\text{P}$  spectra.

For the tetracoordinated complexes of general formula  $[\text{Ag}(\text{PPh}_3)_2\text{L}]$  the  $^{109}\text{Ag}$  isotropic chemical shift values keep within 1301–1342 ppm range (Table 2), and even at a low rotation rate of 3 kHz the effect of silver chemical shielding anisotropy is negligible. The  $\delta_{\text{Ag}}$  signals of

compounds **1** and **7** with the trigonal coordinated silver(I) cation are shifted upfield on approximately 200 ppm.

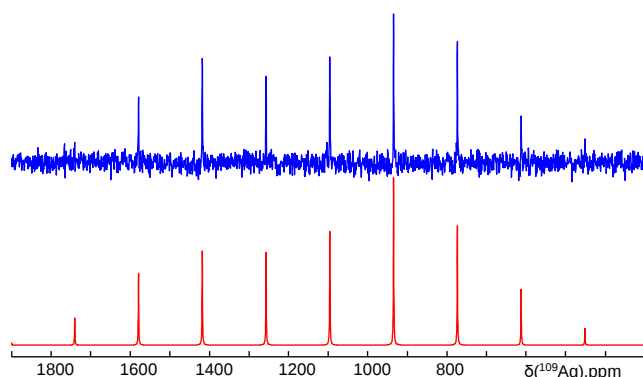


FIGURE 4. Experimental (bleu) and simulated (red),  $^1\text{H}$ - $^{109}\text{Ag}$  solid state CPMAS NMR spectra of complexes  $[\text{Ag}_4\text{L}^{\text{a}}_4]$  **7**.

As stated above,  $^{31}\text{P}$  spectrum contains three lines. Thereby,  $^{31}\text{P}$  NMR data are definitely useful for prediction of only  $[\text{Ag}_3\text{L}_3]$  aggregates formation in the crystal but not the association of the trimeric fragment in the symmetric structures of a higher order. Similar  $^{31}\text{P}$  spectral pattern (like at Figure 3) was observed earlier both for the copper(I) trimer containing in the crystal  $[\text{Cu}_3\text{L}_3]$ ,  $\text{L}=3\text{-MorphC(S)NP(S)(OPr-}i\text{)}_2$  cyclic moiety<sup>[27]</sup> and for the copper(I) centrosymmetric hexamer of formula  $[(\text{Cu}_3\text{L}^{\text{c}}_3)_2]$ , which consists of two  $\text{Cu}_3\text{L}^{\text{c}}_3$  cyclic units bonded by two Cu-S bridges via thiophosphoryl sulfur atoms.<sup>[28]</sup> It should keep in mind that in the trimer complex all copper atoms are three coordinated, while in the hexamer the copper/silver atoms have coordination number of 3 and 4. At the low MAS frequency (3 kHz) solid-state  $^1\text{H}$ - $^{109}\text{Ag}$  CP MAS NMR spectrum showed three set of signals due to the strong effect of silver chemical shielding anisotropy (CSA) (Figure 5).  $\text{AgS}_4$  site is more symmetrical and it has a different coordination than  $\text{AgS}_3$  sites. It leads to different values of the CSA and chemical shift, respectively. See, for example, the NMR parameters for the complexes given above **1-6**. We assigned the signal with higher values of chemical shift at 1160 ppm and with lower values of

CSA parameters to  $\text{AgS}_4$  and the rest two signals to  $\text{AgS}_3$  environments. Thus, based on  $^{109}\text{Ag}$  NMR data further association of the trimeric fragment in the symmetric structures of a higher order can be revealed.

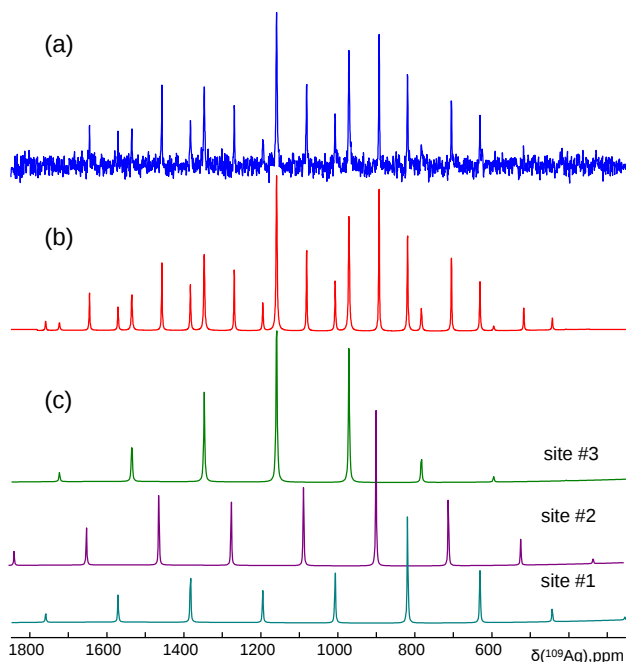


FIGURE 5.  $^{109}\text{Ag}$  CPMAS NMR experimental spectrum of complex  $[\text{Ag}_n\text{L}_n^b]$  **8** (a) and its simulation (b). Decomposition of the theoretical spectrum in its individual components (c).

The silver chemical shift range is a wide and unknown yet for all different environments and all coordination state.  $^{109}\text{Ag}$  chemical shifts obtained in our system for the mixed  $\text{AgS}_2\text{P}_2$  tetrahedral environments range from 1281 ppm to 1358 ppm and for  $\text{AgS}_4$  tetrahedra at 1160 ppm. Berners-Price et al. reported  $^{109}\text{Ag}$  chemical shifts for the different  $\text{AgP}_4$  local environments in the bisphosphine complexes at the high-frequency end of the currently known shift range: 1378–1468 ppm.<sup>[26]</sup> More electronegative phosphorus than sulfur leads to deshielding of Ag and signal appears at downfield. Fijolek et al. studied  $\text{AgS}_2$ ,  $\text{AgS}_3$ , and  $\text{AgS}_4$  coordinations in silver thiolates and in silver butanethiolate and they found 826 ppm for  $\text{AgS}_2$  and range 950–1230 ppm for  $\text{AgS}_3$ .<sup>[29, 30]</sup> Our measurements show chemical shift values from

1007 ppm to 1096 ppm and 1141 ppm for AgS<sub>3</sub> and AgS<sub>2</sub>P planar trigonal coordination, respectively. To summarize, the silver isotropic chemical shifts tend to increase for increasing coordination state and for more electronegative phosphorus than sulfur environments.

Narula et al. studied silver-substituted yeast metallothionein and found a wide range of <sup>109</sup>Ag chemical shifts, for a protein in which Ag(I) ligation occurs exclusively through cysteine thiolates. They could only assume the presence of mixed Ag(I) coordination numbers.<sup>[31]</sup> Based on our and previous studies the assignment of seven resonances ranged from 790 ppm to 1250 ppm to different coordination state can be provided and number of different Ag(I) sites can be quantified.

## Conclusions

The <sup>31</sup>P and <sup>109</sup>Ag CPMAS NMR data have shown their undoubted usefulness for the studying of the obtained silver(I) chelates in the solid phase. Silver solid state NMR can suggest the structure of polynuclear aggregates or their key structural fragments in the crystalline phase. Based on experimental and on literature data, the silver chemical shift ranges for different P,S-environments and coordination state were established. The overall <sup>1</sup>J(<sup>31</sup>P–<sup>107,109</sup>Ag) and <sup>1</sup>J(<sup>31</sup>P–<sup>109</sup>Ag) values obtained by both <sup>31</sup>P and <sup>109</sup>Ag NMR measurements agree. The knowledge obtained in this study will propel the field of silver NMR and provide new insight into the design of new silver(I) complexes.

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TABLE 1.  $^{31}\text{P}$  isotropic chemical shifts and  $^1J_{\text{P-Ag}}$  and  $^2J_{\text{P-P}}$  coupling constants of Ag complexes.

| compound | $\delta_{\text{iso}}$ , ppm<br>( $\pm 0.1$ ppm) | $^1J(^{31}\text{P}-^{107,109}\text{Ag})$ , Hz<br>( $\pm 2$ Hz) | $^1J_{\text{over}}$ ,<br>Hz | $^2J(^{31}\text{P}-^{31}\text{P})$ , Hz<br>( $\pm 2$ Hz) | Integral<br>intensity, %<br>( $\pm 1\%$ ) |
|----------|-------------------------------------------------|----------------------------------------------------------------|-----------------------------|----------------------------------------------------------|-------------------------------------------|
| <b>1</b> | 56.8 [AgL <sup>a</sup> ]                        | -                                                              | -                           | -                                                        | 50                                        |
|          | 12.8 [PPh <sub>3</sub> ]                        | 497                                                            | 495.6                       | -                                                        | 50                                        |
| <b>2</b> | 61.8 [AgL <sup>a</sup> ]                        | -                                                              | -                           | -                                                        | 33                                        |
|          | 5.4 [PPh <sub>3</sub> ]                         | 353                                                            | 355.3                       | 95                                                       | 32                                        |
|          | -1.6 [PPh <sub>3</sub> ]                        | 285                                                            | 287.3                       | 95                                                       | 35                                        |
| <b>3</b> | 63.6 [AgL <sup>b</sup> ]                        | -                                                              | -                           | -                                                        | 33                                        |
|          | 5.7 [PPh <sub>3</sub> ]                         | 340                                                            | 344                         | 123                                                      | 32                                        |
|          | 1.4 [PPh <sub>3</sub> ]                         | 290                                                            | 295                         | 123                                                      | 35                                        |
| <b>4</b> | 59.1 [AgL <sup>c</sup> ]                        | -                                                              | -                           | -                                                        | 33                                        |
|          | 6.2 [PPh <sub>3</sub> ]                         | 330 ( $^{107}\text{Ag}$ )<br>379 ( $^{109}\text{Ag}$ )         | -                           | 108                                                      | 32                                        |
|          | 4.6 [PPh <sub>3</sub> ]                         | 290 ( $^{107}\text{Ag}$ )<br>331 ( $^{109}\text{Ag}$ )         | -                           | 108                                                      | 35                                        |
|          | 62.1 [AgL <sup>d</sup> ]                        | -                                                              | -                           | -                                                        | 33                                        |
| <b>5</b> | 2.7 [PPh <sub>3</sub> ]                         | 342                                                            | 340                         | 91                                                       | 32                                        |
|          | -4.4 [PPh <sub>3</sub> ]                        | 276                                                            | 280                         | 91                                                       | 35                                        |
| <b>6</b> | 64.5 [AgL <sup>e</sup> ]                        | -                                                              | -                           | -                                                        | 17                                        |
|          | 9.6 [PPh <sub>3</sub> ]                         | -                                                              | 306                         | 125                                                      | 15                                        |

|          |                          |   |     |     |     |
|----------|--------------------------|---|-----|-----|-----|
|          | 6.8 [PPh <sub>3</sub> ]  |   | 346 | 125 | 17  |
|          | 59.3 [AgL <sup>c</sup> ] |   | -   | -   | 17  |
|          | 8.4 [PPh <sub>3</sub> ]  |   | 310 | 125 | 17  |
|          | 4.2 [PPh <sub>3</sub> ]  |   | 353 | 125 | 17  |
| <b>7</b> | 56.1 [AgL <sup>a</sup> ] | - | -   | -   | 100 |
|          | 58.2 [AgL <sup>b</sup> ] | - | -   | -   | 33  |
| <b>8</b> | 57.8 [AgL <sup>b</sup> ] | - | -   | -   | 32  |
|          | 54.9 [AgL <sup>b</sup> ] | - | -   | -   | 35  |

TABLE 2. <sup>109</sup>Ag isotropic chemical shifts and <sup>1</sup>J(<sup>31</sup>P–<sup>109</sup>Ag) coupling constants of Ag complexes.

| Compound | Coordination                    | δ <sub>iso</sub> , ppm<br>(±0.1 ppm) | <sup>1</sup> J( <sup>31</sup> P– <sup>109</sup> Ag),<br>Hz (±2 Hz) | Δ <sub>csa</sub> , ppm<br>(±10 ppm) | η <sub>cs</sub><br>(±0.1) | Integral<br>intensity, % (±<br>1%) |
|----------|---------------------------------|--------------------------------------|--------------------------------------------------------------------|-------------------------------------|---------------------------|------------------------------------|
| <b>1</b> | AgS <sub>2</sub> P              | 1141                                 | 531                                                                | 668                                 | 0.83                      | 100                                |
| <b>2</b> | AgS <sub>2</sub> P <sub>2</sub> | 1358                                 | 308<br>380                                                         | -<br>-                              | -<br>-                    | 100                                |
| <b>3</b> | AgS <sub>2</sub> P <sub>2</sub> | 1331                                 | 317<br>369                                                         | -<br>-                              | -<br>-                    | 100                                |
| <b>4</b> | AgS <sub>2</sub> P <sub>2</sub> | 1301                                 | 330<br>379                                                         | -<br>-                              | -<br>-                    | 100                                |
| <b>5</b> | AgS <sub>2</sub> P <sub>2</sub> | 1342                                 | 301                                                                | -                                   | -                         | 100                                |

|          |                                 |        |     |     |      |      |
|----------|---------------------------------|--------|-----|-----|------|------|
|          |                                 |        | 369 | -   | -    |      |
| <b>6</b> | AgS <sub>2</sub> P <sub>2</sub> | 1280.8 | 329 | -   | -    | 50   |
|          |                                 |        | 372 |     |      |      |
|          | AgS <sub>2</sub> P <sub>2</sub> | 1326.6 | 331 | -   | -    | 50   |
|          |                                 |        | 377 |     |      |      |
| <b>7</b> | AgS <sub>3</sub>                | 1096   | -   | 697 | 0.7  | 100  |
|          | AgS <sub>4</sub>                | 1160   | -   | 460 | 0.63 | 33.1 |
| <b>8</b> | AgS <sub>3</sub>                | 1082   | -   | 742 | 0.55 | 33.6 |
|          | AgS <sub>3</sub>                | 1007   | -   | 765 | 0.39 | 33.3 |