

# Competitive bulk membrane transport and solvent extraction of transition and post transition metal ions using mixed-donor acyclic ligands as ionophores

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Competitive transport experiments involving metal ion transport from an aqueous source phase across a chloroform membrane phase into an aqueous receiving phase have been carried out using a series of open-chain mixed-donor ligands as the ionophore in the organic phase. The source phase contained equimolar concentrations of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II), with the source and receiving phases being buffered at pH 4.9 and 3.0, respectively. Clear transport selectivity for silver(I) was observed in all cases. This was also observed in a series of parallel solvent extraction experiments carried out under similar source and membrane phase conditions. Stability constant data confirm that all these ligands show significant affinity for silver(I) in methanol. An X-ray diffraction study of the silver(I) complex of a tripodal NS<sub>3</sub>-donor ligand from the present series is reported. This complex occurs as two crystallographically independent molecules with both forms having a 1 : 1 silver : ligand ratio. The metal coordination geometry of the first form is distorted tetrahedral, with three coordination sites occupied by the three sulfur atoms of the ligand and the fourth site filled by an oxygen atom of the nitrate anion. The silver ion in the second form is five-coordinate being bound to the ligand's apical nitrogen as well as to its three sulfur donors. The remaining position is again occupied by a nitrate oxygen, with the metal coordination geometry in this case best described as distorted trigonal bipyramidal.

## Introduction

Like the crown ethers, the metal-ion chemistry of the podant ligands derived from open-chain polyethylene glycols has now been investigated in considerable depth, especially towards hard metals such as the alkali and alkaline earths.<sup>1</sup> Aspects of the metal ion chemistry of a range of mixed-donor systems of this type have also been reported in previous studies;<sup>2</sup> the complexation behaviour of systems such as **1–6** incorporating aromatic terminal groups has received particular attention, with emphasis being given to their analytical applications.<sup>3–10</sup>

In an early study, it was shown that the bis(8-quinoliny) podand **5** 'wraps around' a metal cation in a helical manner to yield a pseudo-cavity not unlike those exhibited by many macrocyclic systems<sup>11</sup> and the formation of such a cavity on metal binding has subsequently been shown to be typical of this ligand category. While, in general, cation complexes of podants tend to be of lower stability than related macrocyclic species, in particular cases the flexible nature of a podant might be expected to allow a favourable conformation change that will promote metal uptake or release in membrane transport systems. Indeed, such behaviour may be a factor in nature's choice of related open-chain (polyether) antibiotics for promoting efficient metal ion transport across biomembranes.<sup>12</sup>

There have now been a considerable number of investigations of the transport of transition and post-transition metal cations

through bulk liquid membranes using a wide range of synthetic ionophores. The latter include macrocyclic<sup>13</sup> as well as acyclic derivatives,<sup>4,14,15</sup>

In this study we discuss aspects of the solution chemistry of the interaction of silver(I) with **1–6**; included are the results from competitive seven-metal membrane transport and solvent extraction experiments involving the use of the above podants as ionophores/extractants in the respective organic phases. The crystal structure of the silver(I) complex of **6** is also described.

## Experimental

### Materials

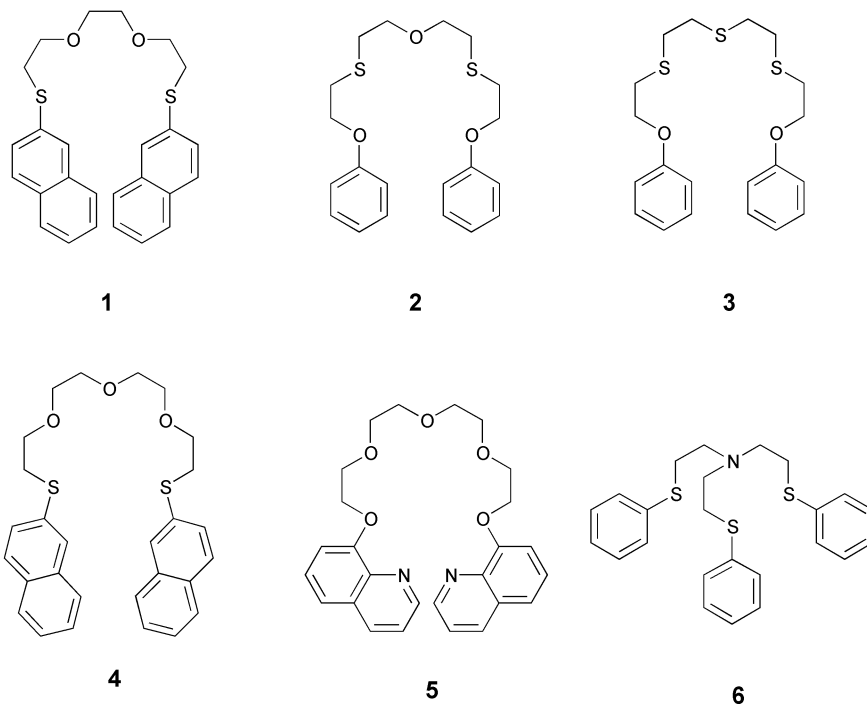
Where available, all reagents were of analytical grade and used without further purification. The acyclic ligands **1**,<sup>5</sup> **2**,<sup>4</sup> **3**,<sup>4</sup> **4**<sup>10</sup> and **6**<sup>3</sup> were prepared and characterised as described previously. Ligand **5** was obtained commercially.

### Preparation of [Ag(**6**)NO<sub>3</sub>]

Silver(I) nitrate (40 mg, 0.234 mmol) was dissolved in methanol (20 ml) and this solution was added to a solution of **6** (100 mg, 0.234 mmol) in methanol (10 ml). The reaction mixture was stirred in the dark for 1 h then filtered. Slow evaporation of the filtrate in the dark afforded colourless crystals. (Found: C, 48.57; H, 4.86; N, 4.75; S, 16.01. Calc. for C<sub>24</sub>H<sub>27</sub>AgN<sub>2</sub>O<sub>3</sub>S<sub>3</sub>: C, 48.40; H, 4.57; N, 4.70; S, 16.15%). FAB mass spectrum: *m/z* 532 for [<sup>107</sup>Ag(**6**)]<sup>+</sup> and 534 for [<sup>109</sup>Ag(**6**)]<sup>+</sup>; IR (KBr/cm<sup>-1</sup>) 3050 (s), 2829 (s), 1578 (s), 1476 (s), 1445 (s), 1380 (NO<sub>3</sub><sup>-</sup>, s), 1304 (s), 747 (s), 691 (s). mp (decomp.) 184–186 °C.

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### Determination of stability constants of silver(I) complexes by potentiometric titration

Log  $K$  values for the silver(I) complexes with **1–6** were determined by potentiometric titration using an  $\text{Ag}^+$ -ISE (Orion 94–16) in methanol at 25 °C. The experimental technique has been described previously.<sup>3,16</sup> The success of these determinations in part reflected the fact that the  $\text{Ag}(\text{I})$ -ISE yielded an essentially Nernstian response in methanol over the silver ion concentration ranges investigated.<sup>3,4,17</sup> The existence of 1 : 1 endpoints in the respective titration curves in each case confirmed the stoichiometries of individual complexes under the conditions employed.

### Membrane transport and solvent extraction

All aqueous solutions were prepared using deionised water. The chloroform used for the membrane phase was presaturated with water by shaking a two-phase water–chloroform mixture then removing the aqueous phase. The transport experiments employed a ‘concentric cell’ in which the aqueous source phase (10 cm<sup>3</sup>) and receiving phase (30 cm<sup>3</sup>) were separated by a chloroform phase (50 cm<sup>3</sup>). Details of the cell design have been reported elsewhere.<sup>18</sup> For each experiment both aqueous phases and the chloroform phase were stirred separately at 10 rpm by means of a coupled single (geared) synchronous motor; the cell was enclosed by a water jacket and thermostatted at 25 °C. The aqueous source phase consisted of a buffer (sodium acetate–acetic acid) solution at pH 4.9 ± 0.1 containing an equimolar mixture of the seven metal ions, each at a concentration of 10<sup>−2</sup> mol dm<sup>−3</sup>. The chloroform phase contained the ionophore at 10<sup>−3</sup> mol dm<sup>−3</sup>. The receiving phase consisted of a buffer (sodium formate–formic acid) solution at pH 3.0 ± 0.1. All transport runs were terminated after 24 hours and atomic absorption spectroscopy was used to determine the amount of each metal ion transported over this period; the respective receiving phases were analysed (using a Varian Spectra AA-800 spectrometer) at the completion of each transport run. The transport results are quoted as the average values obtained from duplicate runs; transport fluxes ( $J$  values) are in mol/24 h and represent mean values measured over 24 h.  $J$  values equal to or less than 20 × 10<sup>−7</sup> mol/24 h are within experimental error of zero and were ignored in the analysis of the results.

Parallel solvent extraction experiments were also performed using identical solutions for the aqueous source phase (2 cm<sup>3</sup>)

and chloroform organic phase (10 cm<sup>3</sup>) to those employed for the corresponding transport experiments. Each two-phase solution in a sealed vial was shaken at 120 cps at 25 °C for 24 h before analysis of the aqueous phase. Metal ion analyses were performed by atomic absorption spectroscopy. Any (apparent) extraction of metal ion of less than 1.5% of the amount originally in the source phase is within experimental error of zero and was ignored in the treatment of the results.

### Crystallographic data collection and structure determination

Data were collected on a Bruker SMART diffractometer equipped with a graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The two-dimensional diffraction images were collected, each of which was measured for 30 s. The frame data were processed to give structure factors using the program SAINT.<sup>19</sup> The structures were solved using a direct method and refined using a full matrix least squares against  $F^2$  for all data using SHELXTL software.<sup>20</sup> All non-H atoms were refined with anisotropic displacement parameters. A summary of data collection parameters is given in Table 1.

CCDC reference number 178304.

See <http://www.rsc.org/suppdata/dt/b2/b200952h/> for crystallographic data in CIF or other electronic format.

### Results and discussion

The stability constants (log  $K$  values) for the 1 : 1 silver(I) complexes of **1–6** in methanol are listed in Table 2. The values in terms of the available donor sets fall in the order:  $\text{S}_3\text{N}$  (**6**) >  $\text{N}_2\text{O}_5$  (**5**),  $\text{S}_3\text{O}_2$  (**3**) >  $\text{S}_2\text{O}_3$  (**2**) >  $\text{S}_2\text{O}_2$  (**4**) >  $\text{S}_2\text{O}_2$  (**1**). Accordingly, the S/N mixed-donor ligand **6** shows stronger affinity for silver(I) than that of the O/N system **5**, with its terminal quinolyl groups, or any of the S/O donor ligands **1–4**. For the latter series, ligand **3** with three soft sulfur donors shows higher affinity for silver than **1**, **2** or **4**, each of which incorporate only two sulfur donors. As discussed elsewhere,<sup>4,21,22</sup> the complex stabilities of such systems are likely dominated by the favourable enthalpic contributions arising from formation of the Ag–S bonds relative to the Ag–O bonds.

**Table 1** Crystal data and structure refinement for Ag(6)NO<sub>3</sub>

Empirical formula	C <sub>24</sub> H <sub>27</sub> AgN <sub>2</sub> O <sub>3</sub> S <sub>3</sub>
Formula weight	595.53
Temperature/K	296(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	16.8287(10)
<i>b</i> /Å	17.6542(10)
<i>c</i> /Å	17.2800(10)
$\beta$ /°	92.9140(10)
Volume/Å <sup>3</sup>	5127.2(5)
<i>Z</i>	8
Absorption coefficient/mm <sup>-1</sup>	1.059
<i>F</i> (000)	2432
Reflections collected	33266
Independent reflections	12430 [ <i>R</i> <sub>int</sub> ] = 0.0657]
Absorption correction	SADABS <sup>27</sup>
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	12430/0/605
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.912
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0440, <i>wR</i> <sub>2</sub> = 0.0801
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1571, <i>wR</i> <sub>2</sub> = 0.1088

**Table 2** Stability constants for the AgL<sup>+</sup> complexes of ligands 1–6 in methanol at 25.0 °C

Ligand	Donor-system	Log <i>K</i>
<b>1</b>	S <sub>2</sub> O <sub>2</sub>	5.55 <sup>a</sup>
<b>2</b>	S <sub>2</sub> O <sub>3</sub>	6.29 <sup>a</sup>
<b>3</b>	S <sub>3</sub> O <sub>2</sub>	7.65 <sup>a</sup>
<b>4</b>	S <sub>2</sub> O <sub>3</sub>	6.00
<b>5</b>	N <sub>2</sub> O <sub>5</sub>	7.69
<b>6</b>	S <sub>3</sub> N	9.29 <sup>b</sup>

<sup>a</sup> Ref. 4. <sup>b</sup> Ref. 3.

Although not quite structural analogues, it is perhaps of interest to compare the relative affinities of **2** (log *K*; 6.29) for silver with those for **1** (log *K*; 5.55) and **4** (log *K*; 6.00). Ligand **2** with its two sulfur donors located in the 'centre' of the aliphatic chain yields a stronger complex than either **1** or **4** in which the sulfurs are adjacent to electron-withdrawing (terminal) aromatic rings.

### Comparative membrane transport and solvent extraction experiments

Competitive mixed-metal transport experiments (water–chloroform–water) employed an organic phase containing the ionophores 1–6 at 10<sup>-3</sup> mol dm<sup>-3</sup>. The aqueous source phase contained equimolar concentrations (each 10<sup>-2</sup> mol dm<sup>-3</sup>) of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) nitrate. As mentioned in the Experimental section, the source and receiving phases were buffered at pH 4.9 and 3.0, respectively. The metal concentration in the aqueous receiving phase was determined on termination of each experiment after 24 hours. Parallel solvent extraction experiments were also carried out for all ligand systems employing an aqueous source phase and chloroform phase that were identical to those used for the corresponding transport experiments. In this case the loss of metal ion from the source phase was determined at the end of each run.

Under the conditions employed, a common feature of all the studies based on 1–6 is the high transport (Table 3) and solvent extraction (Table 4) selectivity for silver(I) relative to the other six metals presented in the respective source phases. Transport efficiency (and selectivity) across bulk liquid membranes has long been known to be influenced by a range of both kinetic and thermodynamic factors.<sup>23</sup> For example, slow kinetics and/or thermodynamic stabilities that are either too low to permit uptake of a metal into the organic phase, or too high to allow

**Table 3** Transport fluxes for silver(I) in seven-metal competitive transport across a bulk chloroform membrane employing 1–6 as ionophores (25 °C)<sup>a,b,c</sup>

Ionophore	Flux
<b>1</b>	228 × 10 <sup>-7</sup>
<b>2</b>	348 × 10 <sup>-7</sup>
<b>3</b>	331 × 10 <sup>-7</sup>
<b>4</b>	115 × 10 <sup>-7</sup>
<b>5</b>	285 × 10 <sup>-7</sup>
<b>6</b>	232 × 10 <sup>-7</sup>

<sup>a</sup> Equimolar concentrations of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) were initially present in the aqueous source phase, each metal had a concentration of 0.01 M, prepared in a buffer solution (CH<sub>3</sub>COOH/CH<sub>3</sub>COONa) pH 4.9. Under the conditions employed (see Experimental), sole transport of silver into the aqueous receiving phase was observed in each case. <sup>b</sup> All values correspond to mol/24 h. <sup>c</sup> Values are the mean from duplicate experiments; typically, errors were less than ±10%.

**Table 4** Percentage extraction of silver(I) in seven-metal competitive extraction (water–chloroform) employing 1–6 as extractants (25 °C)<sup>a,b,c</sup>

Metal ion extraction (%)	
Ligand	Silver(I) extraction (%)
<b>1</b>	15.8
<b>2</b>	25.2
<b>3</b>	23.1
<b>4</b>	2.5
<b>5</b>	10.6
<b>6<sup>b</sup></b>	42.2

<sup>a</sup> Equimolar concentrations of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) were initially present in the aqueous source phase, each metal had a concentration of 0.01 M, prepared in a buffer solution (CH<sub>3</sub>COOH/CH<sub>3</sub>COONa) pH 4.9. <sup>b</sup> Under the conditions employed (see Experimental), except for the system based on **6** (see next footnote), only silver was extracted into the organic phase in each case. <sup>c</sup> For this system, 2.9% of cadmium(II) was also extracted along with silver.

its loss to the receiving phase, will all inhibit transport efficiency and also affect selectivity. An increase in lipophilicity of the ionophore may also increase the efficiency of uptake of a metal salt from an aqueous source phase but also retard its transfer to the (aqueous) receiving phase. Many of these factors (for example, lipophilicity and thermodynamic stability considerations) will also influence extraction efficiency in corresponding two phase solvent extraction experiments. The selectivity for silver observed across all extraction and transport experiments strongly suggests that the origins of such behaviour in the case of the transport experiments is largely the selective transfer of silver across the source phase/membrane phase interface.

For the present systems the NS<sub>3</sub>-donor tripodal ligand **6** shows the highest thermodynamic stability for silver (Table 2) and also exhibits the highest extraction efficiency for this ion (a trace of cadmium is also extracted). For this system 42% of the silver originally in the source phase was extracted (given the relative volumes and concentrations of the source and organic phases, the theoretical maximum that might be attained for 1 : 1 complexation is 50%). Thus, the log *K* value for the silver complex appears to dominate in promoting the passage of silver from the aqueous to the organic phase in this case. In contrast, the transport experiment involving **6** yielded a *J* value for silver ion transport that lies intermediate in the range observed for 1–5 (Table 3). Such behaviour is perhaps best explained by assuming that the substantial thermodynamic stability of the silver complex of **6** strongly aids its transfer into the chloroform phase (see above) while simultaneously (partially) inhibiting its loss from the membrane to the aqueous receiving phase.

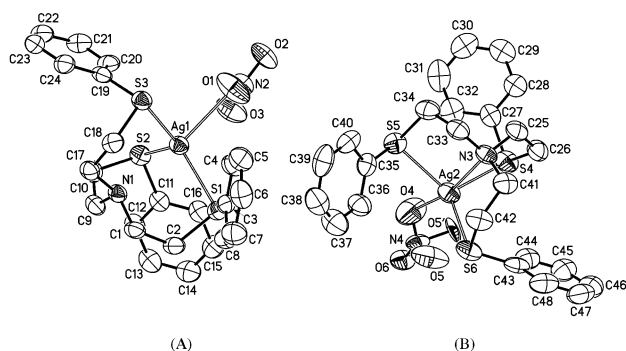
**Table 5** Selected bond lengths (Å) and angles (°) for Ag(6)NO<sub>3</sub>

Molecule A			
Ag(1)–O(1)	2.578(4)	Ag(1)–S(1)	2.5948(12)
Ag(1)–S(2)	2.6134(13)	Ag(1)–S(3)	2.6213(12)
O(1)–Ag(1)–S(1)	103.72(13)	O(1)–Ag(1)–S(2)	119.34(11)
S(1)–Ag(1)–S(2)	113.94(4)	O(1)–Ag(1)–S(3)	82.72(10)
S(1)–Ag(1)–S(3)	116.73(4)	S(2)–Ag(1)–S(3)	116.30(4)
Molecule B			
Ag(2)–O(4)	2.528(4)	Ag(2)–N(3)	2.575(4)
Ag(2)–S(5)	2.6156(15)	Ag(2)–S(6)	2.6313(15)
Ag(2)–S(4)	2.6698(15)		
O(4)–Ag(2)–N(3)	164.52(17)	O(4)–Ag(2)–S(5)	92.10(13)
N(3)–Ag(2)–S(5)	78.99(10)	O(4)–Ag(2)–S(6)	116.82(15)
N(3)–Ag(2)–S(6)	78.65(10)	S(5)–Ag(2)–S(6)	118.32(5)
O(4)–Ag(2)–S(4)	94.32(18)	N(3)–Ag(2)–S(4)	78.32(10)
S(5)–Ag(2)–S(4)	114.81(5)	S(6)–Ag(2)–S(4)	115.55(5)

The observed *J* values for silver ion transport by the remaining ionophores **1–5** show the following order: **2** (S<sub>2</sub>O<sub>3</sub>) ≅ **3** (S<sub>3</sub>O<sub>2</sub>) > **5** (N<sub>2</sub>O<sub>5</sub>) > **1** (S<sub>2</sub>O<sub>2</sub>) > **4** (S<sub>2</sub>O<sub>3</sub>). All are effective transporters of silver into the respective receiving phases — with efficiencies that are somewhat higher than found recently for this ion under similar conditions using mixed nitrogen–sulfur donor macrocyclic ionophores.<sup>24</sup> However, in the absence of additional data concerning such factors as the relative lipophilicity (and associated solvation influences) of these systems and their complex ion species,<sup>22</sup> it is difficult to speculate further concerning the origins of the above order.

### Synthesis and crystal structure of [Ag(6)(NO<sub>3</sub>)]

Since ligand **6** yields the strongest complex of the present series with silver(I) and also acts as its most efficient extractant, the corresponding solid complex was synthesised and its crystal structure determined by X-ray diffraction analysis. Reaction of silver(I) nitrate with one molar equivalent of **6** in methanol yielded colourless crystals that proved suitable for crystallography. Microanalysis data and a fast atom bombardment (FAB) mass spectrum confirmed the stoichiometry of this product to be Ag(6)NO<sub>3</sub>. The results of an X-ray diffraction study are shown in Fig. 1, with selected structural parameters

**Fig. 1** X-Ray structures of the two forms of Ag(6)NO<sub>3</sub>.

listed in Table 5. The unit cell contains two crystallographically independent molecules A and B.

In molecule A, the coordination geometry of the silver atom is distorted tetrahedral with three coordination sites being occupied by the sulfur atoms of **6** [Ag(1)–S(1); 2.595(1), Ag(1)–S(2); 2.613(1) and Ag(1)–S(3); 2.621(1) Å] and the fourth site occupied by an oxygen atom of the NO<sub>3</sub><sup>–</sup> ion [Ag(1)–O(1); 2.578(4) Å]. Each of the silver to sulfur bonds is marginally shorter than the mean (2.675 Å, with standard deviation 0.015 Å) of 51 such bonds taken from the X-ray literature. The largest deviations from tetrahedral coordination around Ag(1) involve the angles O(1)–Ag(1)–S(3) [82.7(1)°] and O(1)–Ag(1)–

S(2) [119.3(1)°]. This distortion may reflect, at least in part, the presence of an additional long interaction (2.648 Å) between the ligand's bridgehead nitrogen N(1) and Ag(1) (see Fig. 1).

Ag(2) in molecule B is effectively five-coordinate with the coordination geometry best described as a distorted trigonal bipyramid. In this case, **6** coordinates *via* a long<sup>25</sup> [2.575(4) Å] Ag(2)–N(3) bond as well as *via* its three sulfur donors (all at unremarkable Ag–S distances), with the latter defining the equatorial plane. The axial positions are occupied by N(3) as well as by O(4) from the nitrate ion [O(4)–Ag(2)–N(3); 164.5(2)°]. Ag(2) is displaced 0.519(1) Å out of the equatorial plane towards the nitrate ion.

### Concluding remarks

Even though the efficiency of both the transport and extraction processes varies considerably from podant to podant, excellent selectivity for silver(I) is maintained across all the present systems in both the membrane transport and solvent extraction experiments. Such behaviour, when taken together with the evidence from the stability measurements and the X-ray diffraction study of Ag(6)NO<sub>3</sub>, are in accord with it being largely the presence of the soft thioether donors in each of **1–6** that dominates the observed selective behaviour. Nevertheless, the possibility of other solution contributions, such as from direct  $\pi$ -interaction of the ligands' aryl rings with silver,<sup>26</sup> can not be ruled out on the available evidence.

### Acknowledgements

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