

## Supplementary Information

Ariel Adamski,<sup>a</sup> Marta A. Fik,<sup>a</sup> Maciej Kubicki,<sup>a</sup> Zbigniew Hnatejko,<sup>a</sup> Dorota Gurda,<sup>b</sup> Agnieszka Fedoruk-Wyszomirska,<sup>b</sup> Eliza Wyszko,<sup>b</sup> Dariusz Kruszka,<sup>c</sup> Zbigniew Dutkiewicz<sup>c</sup> and Violetta Patroniak<sup>a\*</sup>

Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89B, Poznań, 61-614, Poland,  
E-mail: [violapat@amu.edu.pl](mailto:violapat@amu.edu.pl) (V.Patroniak)

Institute of Bioorganic Chemistry, Polish Academy of Science, Noskowskiego 12/14, Poznań, 61-704, Poland

Department of Chemical Technology of Drugs, Poznań University of Medical Sciences, Grunwaldzka 6, Poznań, 60-780, Poland

### <sup>1</sup>H NMR studies

<sup>1</sup>H NMR spectroscopic analysis of an individual ligand **L**, used for the synthesis of complexes, was performed in CDCl<sub>3</sub>, whereas the testing of complexes **1-4** was performed in mixture of deuterium oxide with the addition of 2% of DMSO-*d*<sub>6</sub> which was used as the medium in biological studies.

The <sup>1</sup>H NMR spectrum of free ligand **L** shows the presence of a set of seven signals in the range  $\delta$  8.69–2.69 ppm, assigned to 18 protons in ligand molecule (Fig. S1, S2). The most upfield protons in the ligand spectrum appear as one sharp singlet at  $\delta$  = 2.69 ppm which is generated by six protons assigned to both methyl groups of ligand **L**. 2,2';6',2'';6'',2'''-quaterpyridine scaffold generates the set of six signals in aromatic region, from which each one is assigned to two protons. There are two triplets at  $\delta$  = 8.00 ppm (the value of coupling constant is  $J$  = 7.82 Hz) and at  $\delta$  = 7.78 ppm ( $J$  = 7.73 Hz) and assigned to protons **B** and **E**, respectively. Two doublets, having the same value of coupling constants ( $J$  = 7.82 Hz), are centered at  $\delta$  = 8.45 ppm and at  $\delta$  = 8.50 ppm, thus they were assigned to protons **F** and **D**, respectively. The interaction between protons **D** and **C** are the strongest, as the result of steric hindrance. Consequently, protons **C** generate one doublet at  $\delta$  = 8.66 ppm ( $J$  = 7.73). The most upfield doublet in aromatic region is centered at  $\delta$  = 7.21 ppm and assigned to **A** protons.

The intensity of signals in the spectra of complexes **1-4** is proportional to the number atoms of hydrogen in ligand **L** both in aromatic as well as aliphatic region. In aliphatic region each complex (**1-4**) generates one sharp singlet centered at  $\delta$  = 1.8 ppm, which is assigned to 12 protons derived from four methyl groups of coordinated ligand molecules. The upfield shift of signal from methyl groups in complexes in comparison to free ligand **L** is about  $\Delta\delta$  = 0.9 ppm, what is the result of the complexation process. The same effect of signals shielding is observed in aromatic region for each system **1-4**. A set of five signals is presented, which corresponds to 24 protons from two quaterpyridine scaffolds in helical architectures.

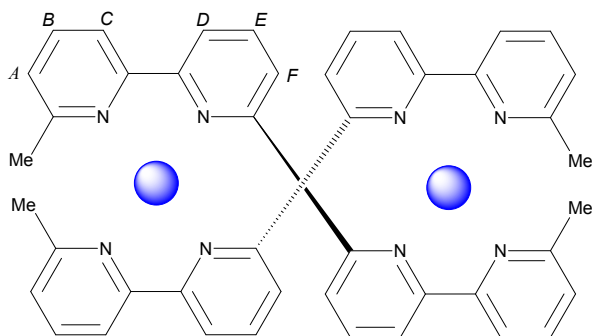
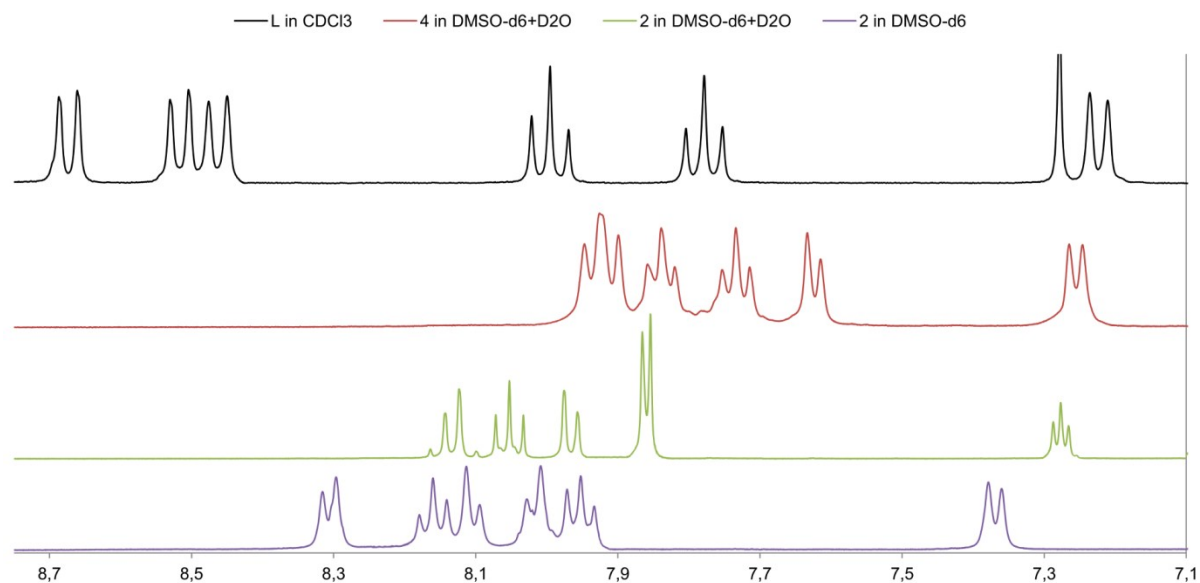


Fig. S1 Schematic representation of complexes **1-4** with atoms labeling.



**Fig. S2** Schematic representation of  $^1\text{H}$  NMR spectra of the ligand **L** as well as complexes **2** and **4**.

The distribution and multiplicity of signals in the spectra of both silver(I) complexes **1** and **2** are nearly identical (a slight difference in the shift of signals amounting to  $\Delta\delta = 0.03$  ppm). The most upfield signal in aromatic region of silver(I) complexes appears as one triplet at  $\delta = 7.27$  ppm ( $J = 4.29$  Hz), which is assigned to four *B* protons. The second triplet in aromatic region is centered at  $\delta = 8.05$  ppm and assigned to four *E* protons. The most downfield signal appears as one doublet at  $\delta = 8.13$  ppm, which has a similar value of coupling constants to doublet of *E* protons, therefore it was assigned to four *F* protons. One doublet at  $\delta = 7.96$  ppm is generated by four protons *A*, for which the value of coupling constants ( $J = 7.55$  Hz) is similar to the ones in free ligand **L**. Interactions in helical structure of silver complex between neighboring protons *C* and *D* gives rise to one sharp doublet at  $\delta = 7.85$  ppm, which corresponds to 8 protons in complex. What is interesting, the NMR spectra of the same silver complex, performed in pure DMSO- $\text{d}_6$ , shows the presence set of six separate signals in aromatic region, which the distribution is similar to the ones in the spectrum of the free ligand. The downfield shift of both triplets and the separation of doublets derived from protons *C* and *D* suggests the cleavage of the helical structure and the formation of mononuclear complex in the presence of such strongly coordinating solvent as DMSO. The integration of signals from ligand and DMSO- $\text{d}_6$  might suggest the equimolar contribution of the ligand **L** and DMSO molecules in coordination sphere of silver(I) complex. It should be noted that solvent with weaker propensity to coordination such as methanol, was found not to disrupt helical structure (*cf.* ESI-MS spectra).

The spectra of both copper(I) complexes **3** and **4** are almost identical with a slight difference in the shift of signals of *ca.*  $\Delta\delta = 0.04$  ppm. The most upfield signal in aromatic region appears as one doublet at  $\delta = 7.25$  ppm and was assigned to four protons in position *A*. Second doublet at  $\delta = 7.62$  ppm is generated by four protons *F*. Two triplets centered at  $\delta = 7.84$  ppm and at  $\delta = 7.73$  ppm were assigned to protons in position *B* and *E*, respectively. The planar surface of bipyridine units of ligand **L** in the complex results in strong interaction between protons *C* and *D*, which gives rise to two overlapping doublets, thus resembling triplet response.

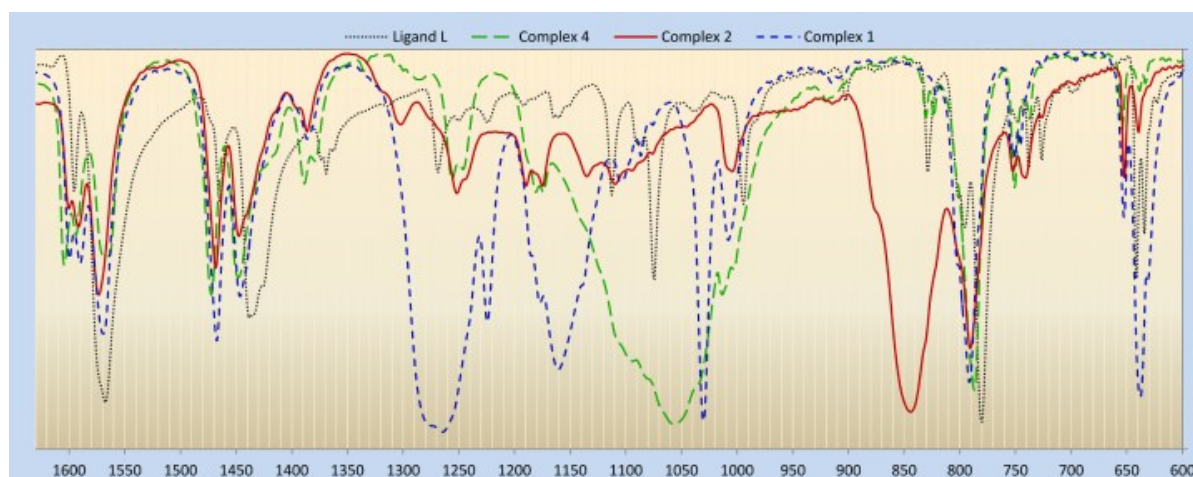
The nature of  $^1\text{H}$  NMR spectra performed for each of complex **1-4**, shows very clearly the stability of the helical form in two percent aqueous DMSO solution, what was crucial to determine the effect of helicity on biological properties.

#### FT-IR Studies

All complexes were found to be the hygroscopic what we can conclude by the presence of the broad bands with small intensity between  $3300\text{ cm}^{-1}$  and  $3680\text{ cm}^{-1}$ , assigned to O-H stretching vibrations of water.

The stretching vibrations of C-H bands are arranged just above as well as just below of  $3000\text{ cm}^{-1}$  value, what is dependent on the carbon hybridization. Thus, the aliphatic protons from methyl groups of free ligand **L** and its complexes **1-4** give rise to bands centered in narrow region at  $2915\text{--}2919\text{ cm}^{-1}$ . On the

other hand, the aromatic protons of each complex generate bands in the region  $3080\text{--}3071\text{ cm}^{-1}$ , which are shifted towards higher wavenumbers in compared with the same ones from free ligand **L**, appearing at  $3056\text{ cm}^{-1}$ . The same effect of bands shifting to higher frequency is observed in the range of C-H out of plane of aromatic rings, where the strong band at  $780\text{ cm}^{-1}$  from free ligand **L** is moved to ca.  $789\text{--}792\text{ cm}^{-1}$  after complexation. Just below them is another group of C-H<sub>oop</sub> bands in the region  $742\text{--}755\text{ cm}^{-1}$  (indicating 2,6-disubstituted pyridine rings) as well as in region  $632\text{--}655\text{ cm}^{-1}$ . All that groups of C-H bonds derived from complexes **1–4** are shifted to higher frequency, what confirms the coordination of ligand **L** (Fig. S3).

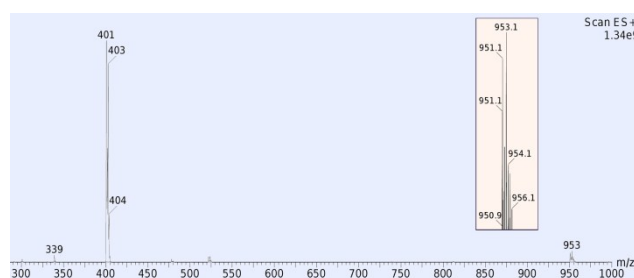


**Fig. S3** Schematic representation of FT-IR spectra of the ligand **L** as well as complexes **1**, **2** and **4**.

The most prominent changes in the pyridine system concern the features in the region between  $1600\text{ cm}^{-1}$  and  $1425\text{ cm}^{-1}$ . In the spectrum of free ligand **L** two C=C stretching bands at  $1599\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$  are present as well as two strong overlapping vibrations centered at  $1568\text{ cm}^{-1}$  and  $1438\text{ cm}^{-1}$  which were assigned to C=C and C=N stretching features. In the spectra of each of complex all that bands are shifted towards higher frequency (by comparing them with the IR spectra of the free ligand) what confirm the ligand coordination. Complexation of related polypyridine ligands is expected to result in shift of C=C and C=N bands towards lower wavenumbers.<sup>1</sup> We have unexpectedly observed IR responses shifted towards higher energy regions and tentatively assign them as an indication of the presence of helical architecture. In addition the band of free ligand at  $1599\text{ cm}^{-1}$  splits into two components for each of complex, what might as well be related with the helical form of complexes.

The nature of the IR spectra of the ligand **L** and its complexes **1–4** is very similar, especially in the range of  $3800\text{--}1300\text{ cm}^{-1}$ , where we can observe only subtle shifts of individual bands of each of complex with respect to frequency of the ligand. Below this region there are numerous strong bands derived from counterions of complexes. Due to the presence of the same counterion in structure of complexes **1** and **3**, the nature of their IR spectra is almost identical in whole the range. Trifluoromethanesulfonate ion gives rise to strong features around  $1265$ ,  $1225$ ,  $1161$ ,  $1030$  and  $1010\text{ cm}^{-1}$  which are the result of the vibration of C-F, C-S and S=O bonds. On the other hand, hexafluorophosphate ion from complex **2** generates bands at  $845\text{ cm}^{-1}$  and  $558\text{ cm}^{-1}$  further assigned as P-F vibrations. The tetrafluoroborate ion of complex **4** gives rise to very broad and strong band at  $1058\text{ cm}^{-1}$  as well as small one at  $522\text{ cm}^{-1}$ . The nature of bands from counterions in the spectra of complexes **1–4** shows their non-coordinating character.

## ESI-MS Spectrum



**Fig. S4** ESI-MS spectrum of complex **3**; the inset presents the isotopic distribution of  $[\text{Cu}_2\text{L}_2(\text{CF}_3\text{SO}_3)]^+$  peak.

<sup>1</sup> M. Wałęsa-Chorab, A. R. Stefankiewicz, A. Gorczyński, M. Kubicki, J. Kłak, M. J. Korabik and V. Patroniak, *Polyhedron*, 2011, **30**, 240.