



Thermodynamics of complex formation of silver(I) with substituted pyridines and cyclic amines in non-aqueous solvents

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Received: 8 August 2023 / Accepted: 12 January 2024
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Abstract

The understanding of the thermodynamic stability and speciation of metal complexes in solution requires access to their enthalpy and entropy of formation. In this work, we specifically focus our investigation on the complexation process of silver(I) ion in acetonitrile (AN) with substituted mono pyridines and cyclic monoamines. The aim of this study is to provide reliable thermodynamic data to obtain insights on metal complex formation, focusing on ligands donor properties and solvation effects. Carefully designed potentiometric and calorimetric experiments allowed to define the species present at different ligand/metal ratios and to obtain the complex formation constants and enthalpies. In general, the enthalpy terms associated with the complex formation are highly exothermic, while the entropy values are always unfavorable. The formation constants of AgL_j species for the ligands investigated in AN are compared with those previously obtained in dimethyl sulfoxide (DMSO) and water. The trends in stability constants and enthalpy values are discussed in relation to the pK_a data available in the different solvents. Higher pK_a values correspond to greater ligand basicity and result in more stable and more enthalpy stabilized complexes.

Keywords Silver(I) · Amines · Complexation · Solvation · Non-aqueous solvents · Thermodynamics

Introduction

Silver coordination in non-aqueous solutions received much interest due to a number of applications ranging from nanomaterial synthesis [1–3], metallic coatings depositions [4, 5], catalysis [6–8], gas separations [9, 10] and electrochemistry [11, 12].

Polyamine N-donor ligands have been shown to be good chelators for silver(I) and other transition or *f*-group cations, both in aqueous [13–19] and non-aqueous solvents [20–26]. In the latter works, the structure and donor properties of the ligand, metal charge, solvation/desolvation processes of the species were analyzed considering the whole thermodynamic parameters of complex formation (ΔG° , ΔH° and ΔS°).

The definition of metal speciation is of paramount importance in water for biomedical, technological and

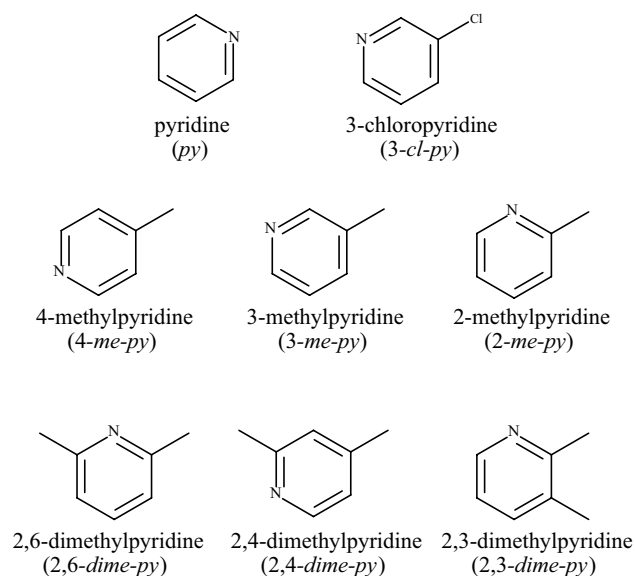
environmental applications [27–32]. However, the understanding of the thermodynamics of solvation and complex formation of metal ions in organic solvents is important for the development of liquid–liquid extraction processes where auxiliary organic complexing agents are often necessary to obtain high selectivity [33–35].

The N-donors affinity for silver(I) was previously investigated in dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and propylene carbonate (PC) [21], and more recently, in acetonitrile (AN), where the thermodynamics of complex formation with some monoamines were obtained [24, 36, 37]. Less data are available about the coordination of sp^2 hybridized nitrogen donors, like pyridines, in AN and the solvent influence on the species involved, despite the coordination chemistry of silver with polypyridyl ligands, in many other solvents, is very rich because of the flexible coordination sphere of this ion and its ability to form, both in solution and in solid state a variety of architectures [38–42].

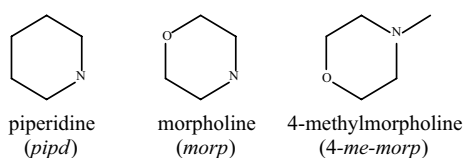
Pyridine-containing ligands also constitute an interesting comparison with amines, as the nitrogen atom is formally tertiary and additional rigidity is provided by the aromatic structure. Due to structural rigidity and lower σ -donor ability than amines [21], a much weaker strength of interaction with

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Scheme 1 Structure of the aromatic amines discussed in this work



Scheme 2 Structure of the heterocyclic amines discussed in this work

metal ions was shown for several transition metal ions and polypyridines in DMSO [43].

In this work, we report the results of a study on the coordination of silver(I) by a series of pyridines in AN to investigate both the effect of steric constraints and of the electron donating/withdrawing properties of the substituents. The pyridines considered are reported in Scheme 1, together with their names and abbreviations used in this work. Data with some non-aromatic cyclic amines (Scheme 2), which are stronger σ -donors than pyridines and rigid at the same time, are also included for comparison. Thermodynamic data obtained for these ligands are compared with those available in water and DMSO which differ from AN for their dielectric constants (ϵ) and donor numbers (DN) [44], with a particular focus on the influence of their acid–base properties on the stability of silver(I) complex formation in the different solvents.

Experimental

Materials

Anhydrous silver perchlorate was obtained by drying $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (Aldrich, Germany) at 323.15 K under

vacuum, the ligands (Aldrich, Germany > 98%) were purified by fractional distillation. AN (Fluka, Germany > 99%) and the background salt (tetraethylammonium perchlorate, NEt_4ClO_4), used to maintain the required 0.1 mol dm^{-3} ionic strength, were purified and dried according to the described procedures [45].

Weighted amounts of the reagents were dissolved in anhydrous AN to prepare the metal and ligand solutions, with the ionic medium adjusted to 0.1 mol dm^{-3} with NEt_4ClO_4 . All the solutions were prepared afresh before use in a MB-150 Braun glove box under atmosphere of dry nitrogen. The water content in the solutions, typically 3–7 ppm, was determined by a Metrohm 684 KF Coulometer.

Potentiometry

All measurements were conducted in a cell maintained at $298.15 \pm 0.1 \text{ K}$ inside a dry box to guarantee the absence of moisture during the measurements. The cell electromotive force (e.m.f.) was measured by means of an Amel 338 pHmeter equipped with a silver Metrohm 6.1248.010 electrode, as a working electrode, and a Metrohm 6.0718.000 reference silver electrode. The Nernstian response of the ion-selective electrode was checked in the $10^{-6} < [\text{Ag}^+] < 10^{-1} \text{ mol dm}^{-3}$ concentration range. Potentiometric experiments were performed by titrating silver perchlorate ($2.0 < C_{\text{Ag}^+}^\circ < 15.0 \text{ mmol dm}^{-3}$ in $V_{\text{cell}} = 20 \text{ mL}$) with solutions of the ligands ($50.0 < C_{\text{L}}^\circ < 200 \text{ mmol dm}^{-3}$ in $V_{\text{burette}} = 5 \text{ mL}$). Titrations were performed with at least three different initial silver(I) ion concentrations, and some of them were carried out in duplicate to verify the reproducibility of the system which was better than 0.4 mV.

The formation constants of the complexes were obtained by using the computer program Hyperquad [46].

Calorimetry

A Tronac model 87–558 precision calorimeter was employed to measure the heats of reaction, with the measure-cell modified in order to be assembled inside the dry box. The response of the calorimeter was checked by titration of tris (hydroxymethyl) aminomethane (THAM) with a standard solution of HCl in water. The experimental value of the standard enthalpy of neutralization of THAM was found to be $\Delta H^\circ = -47.58 \pm 0.20 \text{ kJ mol}^{-1}$, in good agreement with the published value of $-47.53 \pm 0.13 \text{ kJ mol}^{-1}$ [47]. Calorimetric titrations were performed at $298.15 \pm 0.1 \text{ K}$ by adding known volumes of ligand ($V_{\text{burette}} = 5 \text{ mL}$) to silver(I) solutions ($V_{\text{cell}} = 20 \text{ mL}$) with concentrations higher than those used for potentiometry.

In the case of *py*, *3-cl-py* and *4-me-morp*, which formed the weakest complexes among those investigated, the concentration range of metal ion was also extended up to

40 mmol dm⁻³ (and also 80 mmol dm⁻³ for *3-cl-py*) to obtain a more relevant heat signal in the direct titrations. To reach higher ligand-to-metal ratios, also “reverse” calorimetric titrations, were run for all the systems, where the metal ion solution was placed in the burette and the ligand solution in the cell. For the more critical systems, i.e., *3-cl-py*, *4-me-morp* and *py*, the experiments were designed to maximize the formation of ML (*3-cl-py*), or superior ML₂ (*4-me-morp*) or ML₃ species (*py*). For the reverse titrations, 100–280 mmol dm⁻³ solutions of the silver(I) ion ($V_{\text{burette}} = 5 \text{ mL}$) were added to 40–140 mmol dm⁻³ solutions of the ligand ($V_{\text{cell}} = 20 \text{ mL}$). The heats of dilution of the reactants, determined in separate runs, were negligible. The neat reaction heats were used as input data for the cEST program [48] for the calculation of the standard formation enthalpies and Hyss for the speciation calculation [49]. The simultaneous fitting of the stability constants and formation enthalpies of the data of direct and reverse titrations (see results) allowed to determine accurate values of the stability constants and enthalpy values, in agreement with potentiometric data.

Results and discussion

The fitting of the potentiometric and calorimetric data was done considering the following complex formation equilibrium:



where L corresponds to the ligands shown in Tables 1 and 2. The values of j in (1), considered in the speciation models, range from 1 to 3 for all the pyridines (except *3-cl-py* which only forms ML species) and *pipd*, while $j = 1, 2$ for $\text{L} = \text{morp}$ and *4-me-morp*. The formation constants and the corresponding thermodynamic parameters (ΔG_j° , ΔH_j° and $T\Delta S_j^\circ$) are reported in Tables 1 and 2 for pyridines and cyclic amines respectively, together with data available in other solvents [18, 50].

Potentiometric titration data ($\Delta \text{e.m.f. vs. } C_{\text{L}}/C_{\text{Ag}^+}$) are plotted in Fig. 1a–c for silver(I) with *py*, *4-me-py* (representatives of substituted pyridines) and with the cyclic *pipd* amine.

From the analysis of the titration data (Fig. 1a, b), it can be seen that *py* and *4-me-py* does not show a sharp variation in e.m.f values when the $C_{\text{L}}/C_{\text{Ag}^+}$ ratio increases. This is an indication that complex(es) of low stability(es) are formed. All speciation models tested for potentiometric data in the experimental conditions with highest $C_{\text{L}}/C_{\text{Ag}^+}$ did not reveal the formation of AgL₃ species (no improvement of the quality of fitting) both for the other mono- and di-substituted pyridines reported in Table 1. Therefore, only the values of $\log\beta_j$ with $j = 1, 2$, were obtained by potentiometry. For the

system silver(I)-*3-cl-py*, from the potentiometric titrations (Fig. S1) only the AgL species was detected, which reached a maximum of about 21% of presence in our experimental conditions (Fig. S2). Calorimetric experiments, run to obtain enthalpy values, were also designed to check the possible formation of a AgL₃ species (“reverse” titrations, see Experimental) by exploring very high $C_{\text{L}}/C_{\text{Ag}^+}$ ratios. This approach allowed to confirm the presence of AgL₃ species for all systems except *3-cl-py* (Table 1, vide infra). In Fig. S3, it is possible to appreciate how, in the conditions of the potentiometric titrations, the formation of AgL₃ species was too small to be detected.

The results of the calorimetric titrations are shown in Fig. 2a–c, in the form of Δh_v (total reaction heat per mole of metal ion) versus $C_{\text{L}}/C_{\text{Ag}^+}$, for the silver(I)-*py*, *-4-me-py* and *-pipd* systems.

The experimental data for the silver(I)-*py* and *-4-me-py* systems (Fig. 2a,b) agree with what expected on the basis of the potentiometric study. The experimental points are separated for different concentrations of initial silver(I) ion, according to the formation of species of relative low stability. The reverse titrations (Fig. 2a' and b') demonstrate that the separation persists even at higher $C_{\text{L}}/C_{\text{Ag}^+}$ ratios. All the experimental data obtained with direct and reverse titrations were analyzed to obtain $\log\beta_j$ and ΔH°_3 values. In this procedure, the $\log\beta_j$ ($j = 1, 2$), obtained independently by the potentiometric data treatment, were maintained as fixed parameters, while the complexation enthalpies (ΔH_j° , $j = 1–3$) and the $\log\beta_3$ were adjusted to obtain the best fit of data (full lines in the plots). This approach was followed also for the other pyridine systems (except for *3-cl-py*, for which only $\log\beta_1$ and ΔH°_1 were simultaneously fit) and confirmed the existence of three AgL _{j} species. It should be underlined that calorimetric titrations for *3-cl-py* reveal low heat exchange, and for this reason, reverse calorimetric titrations were also run in a wider range of concentrations (up to 140 mmol dm⁻³ of the ligand in cell) to enhance the calorimetric response (Fig. S4).

In the case of cyclic ligands, *pipd* (Fig. 1c) reached the highest $\Delta \text{e.m.f.}$ values both with respect to pyridinic and other substituted cyclic- amines, *morp* and *4-me-morp*, which indicates the formation of more stable complexes than with all pyridine ligands and with *morp* and *4-me-morp*.

The full lines, calculated with the stability constants listed in Tables 1 and 2, are in good agreement with the experimental values.

For silver(I)-*pipd* system, the overlap of the curves up to $C_{\text{L}}/C_{\text{Ag}^+} = 2.0$ indicate the presence of two complexes of similar stabilities ($\log K_1 = 3.45$, $\log K_2 = 3.25$) followed by the formation of a less stable AgL₃ species ($\log K_3 = 0.61$, Table 2). In the latter case, a calorimetric data fitting procedure similar to that described above for the family of pyridines was followed to verify the formation of the AgL₃

Table 1 Overall stability constants and thermodynamic functions (kJ mol^{-1}) for the complex formation between silver(I) and aromatic amines in AN at 298.15 K and $I=0.1 \text{ mol dm}^{-3}$ as defined in reaction (1)

Amine	Solvent	Species	$\log\beta_j$	$-\Delta G_j^\circ$	$-\Delta H_j^\circ$	$-\text{T}\Delta S_j^\circ$
<i>py</i>	AN	AgL	1.70 (2)	9.7 (2)	15.5 (1)	5.8
		AgL ₂	3.02 (2)	17.2 (4)	31.2 (4)	14
		AgL ₃	3.18 (5)	18.2 (3)	55.7 (8)	37.5
<i>3-cl-py</i>	AN	AgL	0.92 (3)	5.3 (2)	10.2 (9)	4.9
<i>4-me-py</i>	AN	AgL	1.98 (2)	11.3 (4)	16 (1)	4.7
		AgL ₂	3.58 (2)	20.4 (2)	33.9 (1)	13.5
		AgL ₃	3.85 (5)	22 (1)	58 (2)	36
<i>3-me-py</i>	AN	AgL	1.87 (3)	10.7 (3)	15.3 (2)	4.6
		AgL ₂	3.32 (3)	18.9 (2)	31.2 (5)	12.3
		AgL ₃	3.69 (7)	21.1 (2)	52.9 (14)	31.8
<i>2-me-py</i>	AN	AgL	1.99 (3)	11.4 (4)	18.3 (33)	6.9
		AgL ₂	3.52 (4)	20.1 (2)	36 (1)	15.9
		AgL ₃	3.85 (13)	22 (2)	55.8 (27)	33.8
<i>2,6-dime-py</i>	AN	AgL	2.05 (4)	11.7 (1)	17.9 (3)	6.2
		AgL ₂	3.44 (6)	19.6 (3)	35.2 (10)	15.6
		AgL ₃	3.7 (3)	21.1 (3)	42 (2)	20.9
<i>2,4-dime-py</i>	AN	AgL	2.27 (3)	13 (2)	18.3 (3)	5.3
		AgL ₂	4.15 (4)	23.7 (1)	36.8 (6)	13.1
		AgL ₃	4.74 (9)	27.1 (4)	54.5 (4)	27.4
<i>2,3-dime-py</i>	AN	AgL	2.10 (7)	12 (2)	16.9 (4)	4.9
		AgL ₂	3.66 (8)	20.9 (2)	35.5 (14)	14.6
		AgL ₃	4.09 (22)	23.3 (5)	53.4 (60)	30.1
<i>py</i>	DMSO	AgL	1.41	8.03	13.9	5.9
		AgL ₂	2.11	12.05	40.9	28.9
<i>py</i>	water	AgL	2.06	11.8	19.2	7.4
		AgL ₂	6.24	35.6	66.1	30.5
<i>4-me-py</i>	water	AgL	2.18	12.4	25.5	13.1
		AgL ₂	6.82	38.9	79.1	40.2
<i>3-me-py</i>	water	AgL	2.25	12.8	21.8	9
		AgL ₂	6.73	38.4	71.5	33.1
<i>2-me-py</i>	water	AgL	2.33	13.3	19.7	6.4
		AgL ₂	6.99	39.9	66.5	26.6
<i>2,4-dime-py</i>	water	AgL	2.54	14.5	–	–
		AgL ₂	7.61	43.4	–	–
<i>2,3-dime-py</i>	water	AgL	2.45	14	–	–
		AgL ₂	7.23	41.3	–	–

In parentheses, an error corresponding to three standard deviations is reported. Data at 298.15 K in DMSO [50] and water [18] are also reported

In ref. [18], $I=0.5 \text{ mol dm}^{-3}$

species for all the cyclic amines. Only AgL and AgL₂ species were detected for *morp* and *4-me-morp*. The excellent fit between calculated and experimental values in Fig. 2 confirms the mutual consistency between the potentiometric and calorimetric measurements.

An improvement of the goodness of fit was obtained when AgL₃ species were included in the models employed in the calorimetric data treatment, in most of the systems investigated (Table 1 and 2). Previous studies carried out in aqueous solution and DMSO [50] showed that these ligands

were able to form only the AgL and AgL₂ species (Table 1 and 2), while the formation of the AgL₃ species is confirmed in this work in AN thanks to the use of reverse calorimetric titrations, which allow to reach high C_1/C_{Ag^+} ratios and thus a significant percent formation (relative to total Ag) of AgL₃ (up to 10% for *py*, up to 13% and 21%, respectively, for the other mono- and di-substituted pyridines and up to 23% for *pipd*, Fig. S5). By using the same calorimetric technique, the AgL₃ species were revealed also for other aliphatic monoamines recently investigated in AN [33].

Table 2 Overall stability constants and thermodynamic functions (kJ mol^{-1}) of silver(I) complexes with heterocyclic amines in AN at 298.15 K and $I=0.1 \text{ mol dm}^{-3}$; estimated three standard deviations in parentheses

Amine	Solvent	Species	$\log\beta_j$	$-\Delta G_j^\circ$	$-\Delta H_j^\circ$	$-\text{T}\Delta S_j^\circ$
<i>pipd</i>	AN	AgL	3.45 (5)	19.7 (2)	25.5 (1)	5.8
		AgL ₂	6.70 (3)	38.2 (4)	58 (2)	19.8
		AgL ₃	7.31 (2)	41.7 (2)	76.6 (2)	34.9
<i>morp</i>	AN	AgL	2.27 (7)	13 (3)	23.4 (4)	10.4
		AgL ₂	4.84 (6)	27.6 (3)	53.5 (6)	25.9
<i>4-me-morp</i>	AN	AgL	1.62 (3)	9.2 (5)	19.1 (2)	9.9
		AgL ₂	2.16 (5)	12.3 (3)	42(1)	29.7
<i>pipd</i>	DMSO	AgL	3.11	17.75	26.30	8.55
		AgL ₂	6.05	34.53	60.40	25.87
<i>morp</i>	DMSO	AgL	2.58	14.73	24.85	10.12
		AgL ₂	4.68	26.71	55.56	28.85
<i>pipd</i>	water	AgL	3.10	17.69	22.18	4.49
		AgL ₂	9.62	54.91	50.20	-4.71
<i>morp</i>	water	AgL	2.25	12.84	-	-
		AgL ₂	7.17	40.92	-	-

Data at 298.15 K in DMSO [50] and water [18] are inserted

In ref. [18], $I=0.5 \text{ mol dm}^{-3}$

The formation of all species is enthalpy stabilized in AN, while the entropy term is always negative, which is characteristic for the formation of metal–ligand covalent bonds and results from the relatively weak solvation of the ligands involved in complex formation and the absence of charge neutralization [20, 21, 51].

The $\log K_1$ values for the aromatic N-donors in AN (Table 1) are lower than those previously reported for primary or secondary monoamines [24]. For example, for *n*-propylamine (*n-pr*), $\log K_1$ was found to be 3.54 with an enthalpy change (ΔH_1°) of $-27.1 \text{ kJ mol}^{-1}$. Additionally, the $\log K_1$ values for these aromatic N-donors are also lower than those obtained for cyclic secondary *pipd* and *morp*. This decrease in $\log K_1$ values can be attributed to the reduced σ -donor ability exhibited by these aromatic N-donors. However, the $\log K_1$ values for the pyridines in Table 1 are closer to the stability observed for *4-me-morp* (Table 2) and tertiary monoamines in general [21, 24]. For instance, the $\log K_1$ value for tripropylamine (*tri-pr*) is 1.66 [24] with an enthalpy change (ΔH_1°) of $-23.2 \text{ kJ mol}^{-1}$. This suggests that the silver(I) complexes with aromatic N-donors present stabilities similar to tertiary monoamines due to their limited σ -donor strength in solution, which is much higher for primary and secondary amines [42]

In addition, the $\log K_1$ for *py* is increasing in the considered solvents in the order: DMSO < AN < water. This trend obtained for *py* is opposite to that obtained for ligands containing primary or secondary amine groups and can be explained by the prevalence of the metal over ligand solvation in DMSO for those who are H-bond acceptors only [21, 43, 52]. Similarly, the formation constants (and the enthalpy values) for all the pyridinic ligands considered here, follow

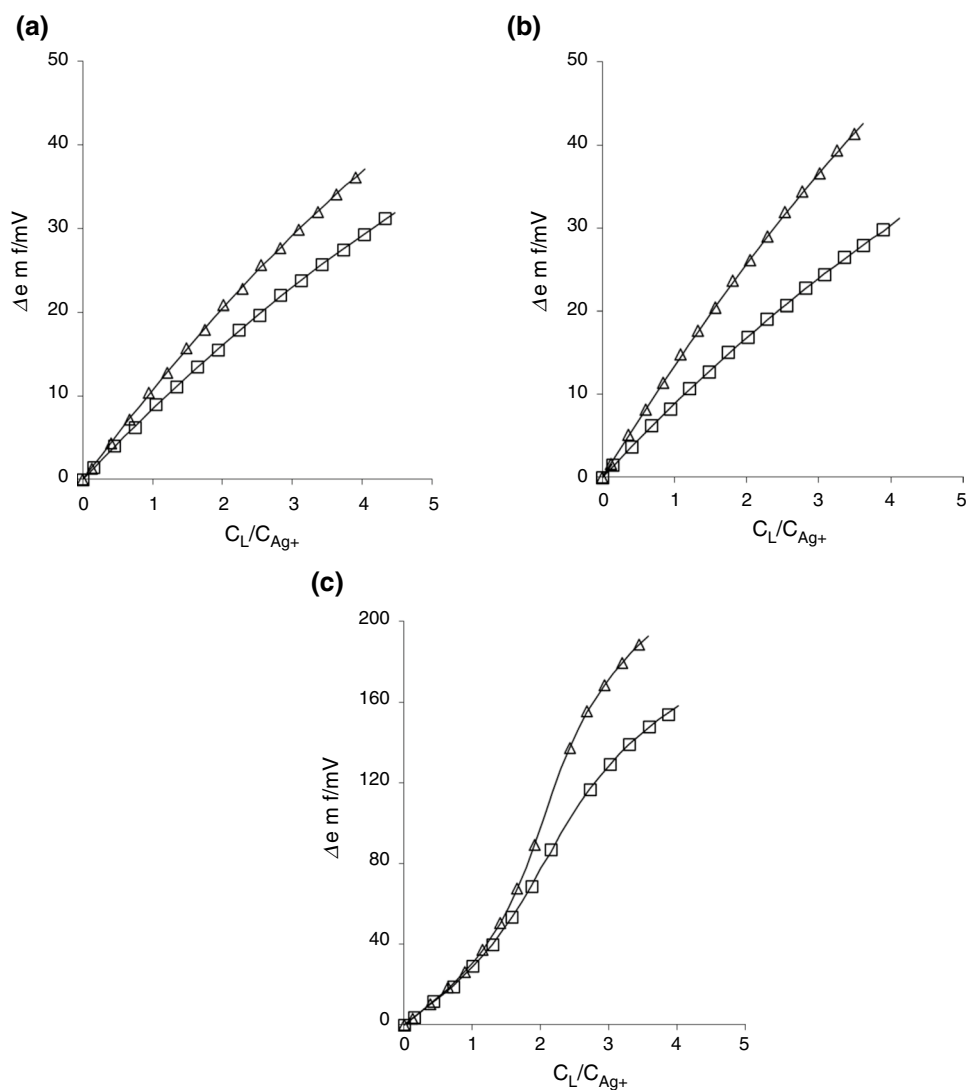
the trend expected on the basis of metal ion solvation (Table 1). The thermodynamic parameters for the metal ion transfer ($\Delta G_{\text{tr}}^\circ$, $\Delta H_{\text{tr}}^\circ$, $\text{T}\Delta S_{\text{tr}}^\circ$) from AN to water and DMSO [53] are reported in Table 3, together with the dielectric constants (ϵ) and donor numbers (DN) of the solvents [44]. The $\Delta G_{\text{tr}}^\circ$ and $\Delta H_{\text{tr}}^\circ$ data show that the solvation strength for silver(I) increases in the order water < AN < DMSO. The enthalpy of solvation of silver(I) is more negative in the aprotic solvents compared to the protic one like water (Table 3). This can be due to the intrinsically stronger Ag-solvent bond with DMSO and AN than water, as shown by gas phase experiments [54] and also to the different solvation structure of the metal ion. In fact Ag(I) is solvated by an average of 4 solvent molecules [55, 56] in DMSO and AN, while a quasi-linear (“2+2”) coordination has been shown in water [32].

As a result, the stability of metal-pyridines complexes follows a trend where the complexes are less stable in the organic solvents than in water due to the differing solvation energies of the silver(I) ion.

As $\text{p}K_a$ values are key parameters defining the acid–base behavior of the ligands in water [57], AN and DMSO [61], these values are documented in Table 4 and referred to the reaction $\text{LH}^+ + \text{S} \rightleftharpoons \text{L} + \text{SH}^+$ (L = ligand, S = solvent). The analysis of these data should be useful to investigate the general trend in stability constants and thermodynamic parameters, not only for *py*, but also for all the other mono- (*4-me-py*, *3-me-py* and *2-me-py*), di-substituted pyridines (*2,4-dime-py*, *2,3-dime-py* and *2,2-dime-py*) and cyclic (*pipd*, *morp* and *4-me-morp*) amines.

In general, it is evident that LH^+ are much weaker acids in AN than in water (and in DMSO) as the difference of the

Fig. 1 Plot of the observed (symbol) and calculated (solid line) $\Delta e.m.f.$ values obtained for silver(I) titrations in AN versus the total ligand-to-metal (C_L/C_{Ag^+}) ratio with: (a) *py* ($C_{Ag^+}^0 = 8.76$ (open square) and $12.14 \text{ mmol dm}^{-3}$ (open triangle)), (b) *4-me-py* ($C_{Ag^+}^0 = 4.53$ (open square) and $9.36 \text{ mmol dm}^{-3}$ (open triangle)) and (c) *pipd* ($C_{Ag^+}^0 = 5.68$ (open square) and $13.87 \text{ mmol dm}^{-3}$ (open triangle))



pK_a values (ΔpK_a) is systematically larger by about 7 (or 9) pH units compared to the corresponding values for water (or DMSO), mainly due to the lower dielectric constant and the weaker basicity of AN, which result in smaller free energy of solvation of LH^+ (or higher solvation of L) in AN than in DMSO and water [61, 70].

DMSO is known for its ability to be a strong hydrogen bond acceptor [71]. In DMSO, primary amines act as stronger bases compared to water, while *pipd* is slightly weaker as a base in DMSO than in water (Table 4). Additionally, pyridine-containing ligands exhibit significantly weaker basicity in DMSO as compared to water [72, 73].

The values of $\log K_1$ versus the corresponding pK_a for the ligands studied in this work in the three solvents (Table 1 and 2) are reported in Fig. 3. Also, the data (taken from ref [24]) relative to the aliphatic secondary monoamine dibutylamine (*di-but*) are inserted in Fig. 3, for comparison with the secondary cyclic *pipd*. For *di-but* data of $\log K_1$ and pK_a are

available in AN and DMSO ($\log K_1 = 3.14, 2.66$, respectively [24]; for pK_a , see Table 4).

In general, it can be observed that $\log K_1$ values increase with increasing in pK_a , in all the solvents considered, in line with an increase in basicity of the ligands, with a little discontinuity on going from the family of pyridines to the amines in water and AN. However, if the pyridines and cyclic amines are considered separately, a nearly linear correlation between pK_a and $\log K_1$ can be appreciated (see below, Fig. S6).

As far as the pyridines are considered, the decrease in pK_a value in the aprotic AN is particularly evident going from *py* to *3-cl-py* ($\Delta pK_a \text{ AN } py \rightarrow 3-cl-py = 2.97$) and parallels the strong decrease already observed in water ($\Delta pK_a \text{ water } py \rightarrow 3-cl-py = 2.25$), which was mainly ascribed to the inductive effect of chloride [67]. Also, the stability of silver(I)-*3-Ccl-py* complex is particularly low as compared to *-py* and certainly related to this inductive effect of the

Fig. 2 Plot of the observed (symbol) and calculated (solid line) total molar enthalpy changes, $-\Delta h_v$, as a function of C_L/C_{Ag^+} for silver(I) titrations in AN. **(a)** *py* ($C_{Ag^+}^\circ = 28.04$ (filled circle) and $39.03 \text{ mmol dm}^{-3}$ (filled triangle)), **(b)** *4-me-py* ($C_{Ag^+}^\circ = 31.34$ (filled circle) and $38.71 \text{ mmol dm}^{-3}$ (filled triangle)) and **(c)** *pipd* ($C_{Ag^+}^\circ = 19.70$ (filled circle) and $29.78 \text{ mmol dm}^{-3}$ (filled triangle)). On the right, reverse titrations are shown: **(a')** *py* ($C_L = 64.23$ (open circle) and $92.51 \text{ mmol dm}^{-3}$ (open triangle)), **(b')** *4-me-py* ($C_L = 60.03$ (open circle) and $85.47 \text{ mmol dm}^{-3}$ (open triangle)) and **(c')** *pipd* ($C_L = 41.72$ (open circle) and $58.73 \text{ mmol dm}^{-3}$ (open triangle))

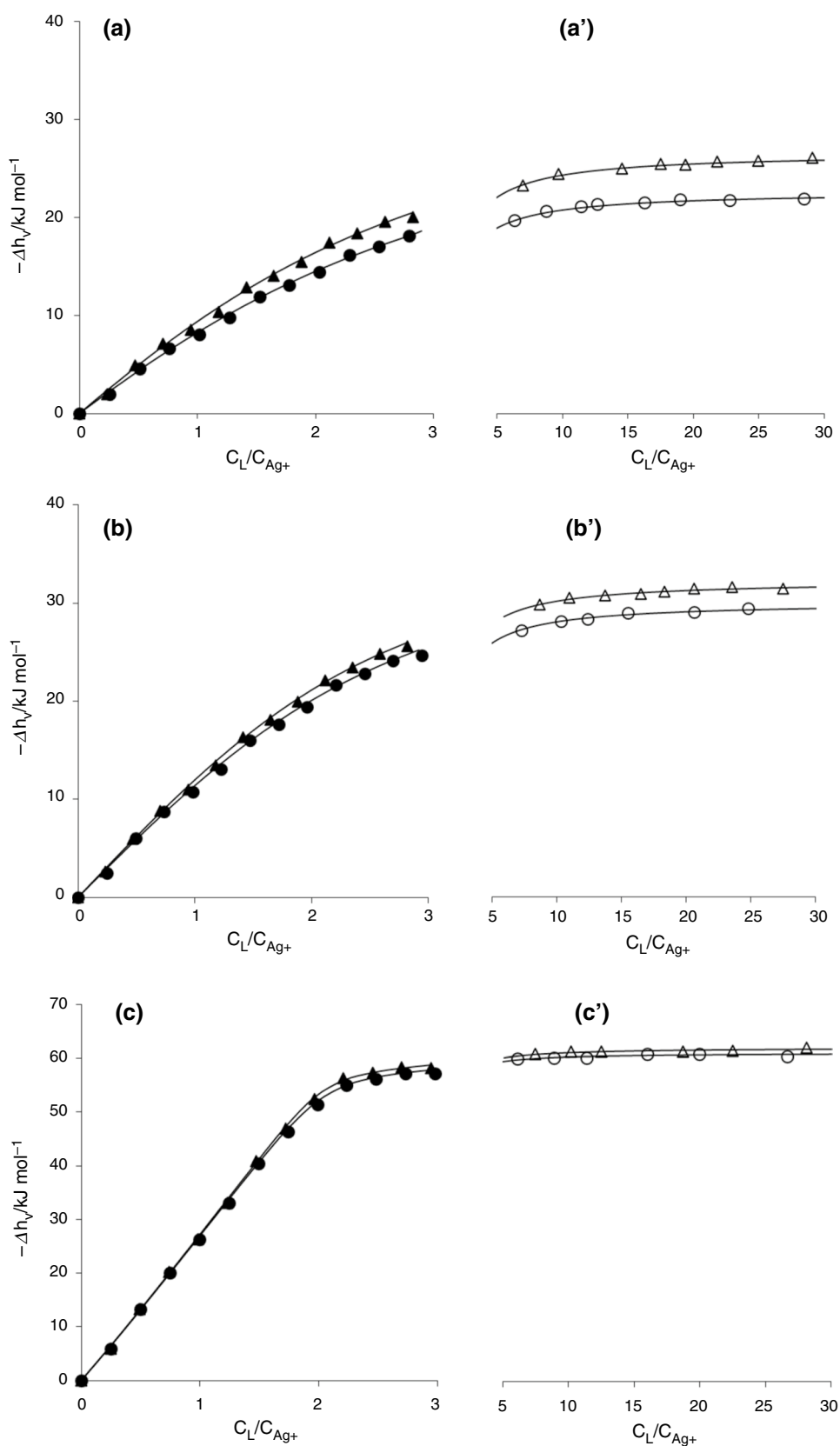


Table 3 Dielectric constants (ϵ) and donor numbers (DN) of some organic solvents with the free energies, enthalpies and entropies of transfer (kJ mol^{-1}) of silver(I) ion from AN to water and DMSO solvent ($\Delta G_{\text{tr}}^{\circ}(\text{AN} \rightarrow \text{solvent})$, $\Delta H_{\text{tr}}^{\circ}(\text{AN} \rightarrow \text{solvent})$ and $T\Delta S_{\text{tr}}^{\circ}(\text{AN} \rightarrow \text{solvent})$, respectively) at 298.15 K

	ϵ^a	DN ^a	$\Delta G_{\text{tr}}^{\circ b}$	$\Delta H_{\text{tr}}^{\circ b}$	$T\Delta S_{\text{tr}}^{\circ b}$
AN	35.94	14.1	–	–	–
Water	78.36	18.0	22.0	41.0	19.0
DMSO	46.45	29.8	–12.0	–10.0	2.0

Values calculated from ref. [44]^a; ref. [53]^b

Table 4 $\text{p}K_{\text{a}}$ data for amines in different media referred to reaction: $\text{LH}^+ + \text{S} \rightleftharpoons \text{L} + \text{SH}^+$

Amine	$\text{p}K_{\text{a}}$ (AN)	$\text{p}K_{\text{a}}$ (DMSO)	$\text{p}K_{\text{a}}$ (H_2O)
<i>py</i>	12.53 ^a	3.4 ^b	5.23 ^c
<i>3-cl-py</i>	9.56 ^a	–	2.98 ^d
<i>4-me-py</i>	–	–	6.0 ^d
<i>3-me-py</i>	–	–	5.7 ^d
<i>2-me-py</i>	13.28 ^a	4.01 ^e	5.9 ^d
<i>2,6-dime-py</i>	14.16 ^a	4.46 ^e	6.7 ^e
<i>2,4-dime-py</i>	14.05 ^f	4.5 ^f	6.79 ^d
<i>2,3-dime-py</i>	–	–	6.59 ^g
<i>pipd</i>	19.29 ^h	10.85 ⁱ	11.22 ^j
<i>morp</i>	16.61 ^k	9.15 ⁱ	8.49 ^l
<i>4-me-morp</i>	15.59 ^f	–	7.38 ^m
<i>di-but</i>	18.31 ^k	10 ^b	11.25 ^j

^a[57]. ^b[58]. ^c[59]. ^d[60]. ^e[61]. ^f[62]. ^g[63]. ^h[64]. ⁱ[65]. ^j[66]. ^k[67]. ^l[68]. ^m[69]

chlorine, which decreases the donor properties of the N atom. In agreement with that effect, also the obtained $\Delta H_{\text{tr}}^{\circ}$ value is rather low as compared to *py*.

On the contrary, when a methyl electron-donor group is inserted, the basicity increases, the $\text{p}K_{\text{a}}$ passing from 12.53 for *py* to 13.28 for *2-me-py* in AN. In water a similar increase of 0.7 $\text{p}K_{\text{a}}$ units is observed. The inductive effect of the electro-donating group is more effective when present in α or γ position [74] and this is also reflected in the $\log\beta_1$ value for *2-me-py* and *4-me-py* which are higher not only with respect to *py* but also to *3-me-py*. The values of $\log K_1$ and $\Delta H_{\text{tr}}^{\circ}$ obtained in this work in AN, together with those for *di-but* [24], as a function of $\text{p}K_{\text{a}}$ are shown in Fig. 4.

It can be clearly noted, that both $\Delta H_{\text{tr}}^{\circ}$ for pyridinic ligands (Table 1) and $\log K_1$ (Table 1) increase along the $\text{p}K_{\text{a}}$, and this is true also for the cyclic amines (Table 2): an exception is found for *2,6-dime-py*, which shows a slightly lower stability, likely due to steric hindrance of the two methyl groups adjacent to the N donor.

In general, within a given family of ligands, a good correlation between $\log K_1$ and $\text{p}K_{\text{a}}$ is obtained (pyridines,

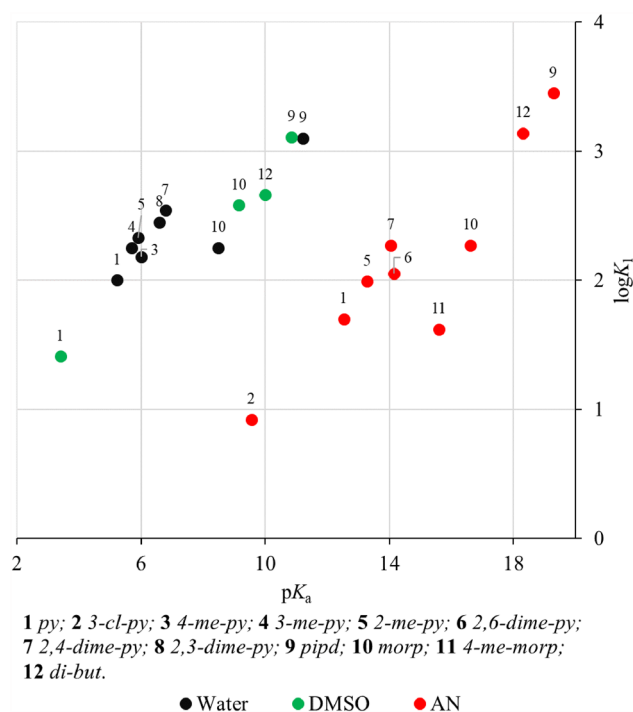


Fig. 3 $\log K_1$ as a function of $\text{p}K_{\text{a}}$ for the studied amines in the different solvents (AN, DMSO and water)

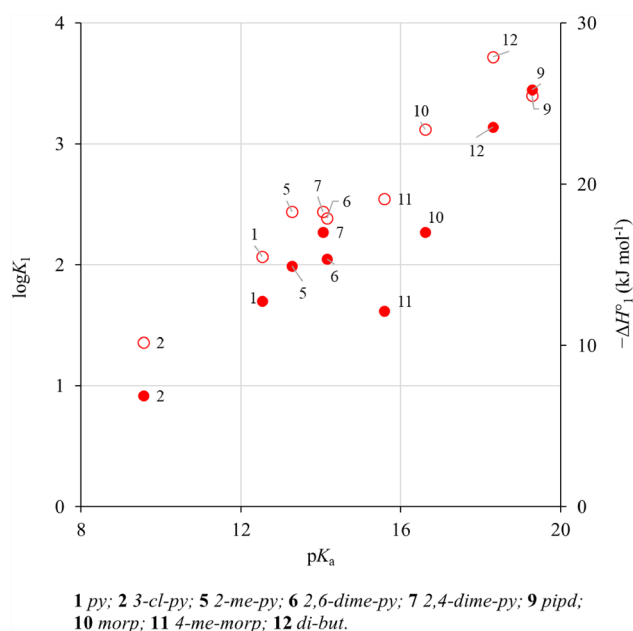


Fig. 4 Values of $\log K_1$ (circles) and $\Delta H_{\text{tr}}^{\circ}$ (empty circles) as a function of $\text{p}K_{\text{a}}$ in AN

$R^2=0.968$ and for cyclic amines $R^2=0.988$), whereas the linearity is less evident when all the ligands in Fig. 4 are considered ($R^2=0.825$, Fig. S6-7). The linear relationship is even better for the $-\Delta H_{\text{tr}}^{\circ}$ vs. $\text{p}K_{\text{a}}$ plot ($R^2=0.937$),

when considering all the ligands, both pyridines and cyclic amines, as can be seen from the interpolation and the relative equation reported in Figure S8. This result supports the strong correlation between the strength of Ag–N bond, mainly reflected in $-\Delta H_1^\circ$ value, and the base σ -donor ability of the N atom.

Moreover, it can be observed that: (i) the cyclic secondary amine *pipd* shows stability and ΔH_1° very close to that of secondary linear ones (for *di-but* $\log K_1 = 3.14$, $\Delta H_1^\circ = -27.9$ kJ mol⁻¹), thus indicating that there are no remarkable influences on complexation, due to the rigidity introduced by the cyclization of the ligand; (ii) the stability of silver(I)-*morp* complex is lower than that of *pipd*, due to a decreased favorable enthalpy term, owing to the electro-attractive properties of the oxygen atom in the cycle which decreases the donor ability of the N atom [75]; (iii) when the methyl group is present on N atom, in *4-me-morp*, the stability of the complex is much decreased: the σ -donor properties of the tertiary nitrogen atom are lowered and the complex solvation energy can be reduced due to the increased size of the species (the larger complex size can provide a greater surface area for interactions with the surrounding solvent molecules, leading to a reduction in solvation energy in some cases) [52, 75]. This agrees with the lower stability and enthalpy of the complex formed and with a more unfavorable entropy effect with respect to *morp*.

The second stepwise stability constant for the formation of silver(I) with the secondary *pipd* and *morp* (Table 2) K_2 , are similar to K_1 in AN. The complete set of thermodynamic functions in AN for the reactions concerning the second complexation step reveals that this stability trend results from a balance between the favorable enthalpy of reaction and unfavorable entropy. The stepwise enthalpy ($-\Delta H_{K2}^\circ > -\Delta H_{K1}^\circ$; that is -32.5 vs -25.5 for *pipd* and -30.1 vs -23.4 kJ mol⁻¹ for *morp*) and entropy trends ($-\Delta S_{K2}^\circ > -\Delta S_{K1}^\circ$, that is -8.8 vs -22.0 for *pipd* and -7.9 vs -18.0 kJ mol⁻¹ for *morp*) can be interpreted as reflecting a greater desolvation occurring at the first step of complexation, which makes ΔH_{K1}° less negative than ΔH_{K2}° , in spite of the certainly greater metal–ligand interaction in the first complexation step. This is in line with the entropy values which, in the second step, are more negative than in the first step. This trend (K_2 similar to K_1 and $-\Delta H_{K2}^\circ > -\Delta H_{K1}^\circ$) is present also in DMSO for the aliphatic *pipd* and *morp*.

For the pyridinic ligands the trend in the values of ΔH_{K1}° and ΔS_{K1}° with respect to ΔH_{K2}° and ΔS_{K2}° is similar, but not so remarkable as for secondary amines *pipd* and *morp*. As a matter of fact, $-\Delta H_{K1}^\circ$ values are lower, in the range 15.5–18.3 kJ mol⁻¹ for the first step and $-\Delta H_{K2}^\circ$ is in the range 15.7–18.3 kJ mol⁻¹, whereas the decrease in ΔS_{K2}° are more significant with respect to ΔS_{K1}° . Thus, the result of the balance between enthalpy and entropy terms always results in $K_2 < K_1$.

Finally, when the AgL₃ species is formed, a low stability is found (Table 1 and 2). The enthalpy associated to the third formation step is close to that found for the other species, whereas the ΔS_{K3}° is much more negative. This agrees with the fact that a strong Ag–N bond is always formed, but unfavorable entropy changes occur, which almost completely compensate the complexation enthalpy.

Conclusions

The complex formation between silver(I) ion and a series of N-donors in AN is characterized by high exothermic enthalpy changes indicating formation of relatively strong Ag–N bonds, while the unfavorable entropy is diagnostic of a decrease in disorder of the system. Carefully designed calorimetric experiments allowed to obtain both stability constants and enthalpy terms and highlighted the presence of species formed at high metal-to-ligand ratios, *i.e.*, AgL₃ in this work.

The $\log K_1$ values (and the negative enthalpy values) for pyridine ligands is increasing in the order: DMSO < AN < water. This stands in contrast to the trend observed for ligands containing primary or secondary amine groups, which are H-bond solvated in DMSO and water and is explained by the prevalence of metal ion solvation on ligand solvation, in the case of pyridine ligands.

This study shows that $\log K_1$ values increase with increasing pK_a values for all considered solvents, indicating that higher pK_a values correspond to greater ligand basicity and in general more enthalpy stabilized complexes. The behavior of the pyridine family in AN, closely resembles that observed in water. Finally, *pipd* exhibits stability and ΔH_1° close to linear secondary amines, suggesting minimal impact on complexation from ligand cyclization.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10973-024-12894-2>.

Acknowledgements Research financed with European Union funds – NextGenerationEU—MSCA grants D.M. 737/2021—CUP G25F21003390007. This work was supported by the University of Udine in the framework of the Strategic Plan 2022-25 – Interdepartmental Research Project ESPeRT.

Author contributions MS done investigation, writing—original draft, review & editing. AK and MC done investigation. AM helped in investigation, writing—original draft, review & editing, formal analysis, supervision, and conceptualization. MT done investigation, writing—original draft, review & editing, supervision, conceptualization, and funding acquisition.

Funding Open access funding provided by Università degli Studi di Udine within the CRUI-CARE Agreement.

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