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Coordination Chemistry Reviews 252 (2008) 1270–1285
COORDINATION CHEMISTRY REVIEWS
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Review

Complex formation of N-donor ligands with group 11 monovalent ions

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Received 25 July 2007; accepted 6 December 2007

Contents

Abstract

Thermodynamic data on complex formation between nitrogen donor ligands (amines, pyridines) and group 11 monovalent ions in water and non-aqueous media are reviewed here. Particular emphasis is paid to Ag(I) complex formation in water and dimethylsulfoxide (DMSO), due to the amount and quality of data available. The influence of different basicities and steric properties of ligands, together with the solvation of the species involved, on the stability and nature of the resulting complexes is discussed. It emerges generally that the coordination properties of amines towards 1+ ions are all modulated through the number and basicity of nitrogen atoms present in the ligand, chelate ring sizes, degree of N-functionalisation, and the nature of the solvent. When possible, the thermodynamic properties of the complexes are related to the structural features of the ligands.

Keywords: Silver(I); Copper(I); Gold(I); N-donor ligands; Basicity; Complexes; Water; Non-aqueous solvents; Thermodynamics

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Abbreviations: **A1**, ammonia; **A2**, methylamine; **A3**, ethylamine; **A4**, 1-aminopropane; **A5**, 1-aminobutane; **A6**, 1-pentylamine; **A7**, hexylamine; **A8**, dimethylamine; **A9**, trimethylamine; **A10**, diethylamine; **A11**, triethylamine; **A12**, methylethylamine; **A13**, dimethylethylamine; **A14**, *N*,*N*-diethylmethylamine; **A15**, dibutylamine; **A16**, tributylamine; **A17**, 2-propylamine; **A18**, 1-amino-2-methylpropane; **A19**, 2-aminobutane; **A20**, dimethylisopropylamine; **A21**, dimethyltertbutylamine; **DA1**, 1,2-diaminoethane; **DA2**, *N*-methyl-1,2-diaminoethane; **DA3**, *N*,*N*′-dimethyl-1,2-diaminoethane; **DA4**, *N*,*N*-dimethyl-1,2-diaminoethane; **DA5**, *N*,*N*,*N*′-trimethyl-1,2-diaminoethane; **DA6**, *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane; **DA7**, 1,3-diaminopropane; **DA8**, *N*,*N*-dimethyl-1,3-diaminopropane; **DA9**, *N*,*N*′-dimethyl-1,3-diaminopropane; **DA10**, *N*,*N*,*N*′-trimethyl-1,3-diaminopropane; **DA11**, *N*,*N*,*N*′,*N*′-tetramethyl-1,3-diaminopropane; **TA1**, 1,4,7-triazaheptane; **TA2**, 1,4,7-triazaoctane; **TA3**, 2,5,8-triazanonane; **TA4**, 7-methyl-1,4,7-azaoctane; **TA5**, 2,8-dimethyl-2,5,8-triazanonane; **TA6**, *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethylenetriamine; **TA7**, 1,5,9-triazanonane; **TRA1**, 1,4,7,10-tetraazadecane; **TRA2**, 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane; **TRA3**, 1,5,8,12-tetraazadodecane; **PA1**, 1,4,7,10,13-pentaazatridecane; **PA2**, 2,5,8,11,14-pentamethyl-pentaazapentadecane; **P1**, pyridine; **BP1**, 2,2′-bipyridine; **AP1**, 2-pyridylamine; **AP2**, 2-(aminomethyl)-pyridine; **TP1**, 2,2′:6′,2″-terpyridine; **BPA1**, (2,2′-dipyridyl)-amine; **BPA2**, bis-((2-pyridyl)methyl))-amine.

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doi:10.1016/j.ccr.2007.12.007

1. Introduction

In the last few decades, a great deal of interest has been devoted to the thermodynamics of complex formation of metal ions with N-donors in water [1–3] and in non-aqueous or mixed solvents [4–13]. The aim of these studies has been to investigate the influence both of different basicity and steric properties of ligands and of solvent media on the stability and nature of the complexes, and to design ligands for selective complexation of metal ions.

In some cases, empirical or theoretical approaches have also been pursued to calculate formation constants or binding energies [14]: the former are of great importance, for example, in water, to understand or predict the role of metal ion complexes in biology [15], their behaviour and speciation in the environment [16] and their possible application in medicine [17].

The values of complexation constants in organic solvents may also be of great help in designing metal-active centres for catalytic applications and in providing basic information on the effect of solvation on complex formation. As regards this last point, knowledge of other thermodynamic quantities (enthalpy and entropy of complex formation) is desirable. This latter field is evidently very wide and rich in data, which should be rationalised in order to find useful correlations between thermodynamic parameters and, for example, steric, electronic and solvation effects of both reagents and resulting complexes.

In several previous studies [4,5,7–10,18–29], we investigated the complexation of transition metal ions and lanthanides with neutral N-donors in aprotic solvents: in this review, we rationalise the information, beginning with thermodynamic parameters relative to group 11 monovalent metal complexation, for which a great amount of data has been collected, especially as regards Ag(I) [2,3,7,9,10,12,20,24,30–44]. This predominance is basically due to the instability of the 1+ oxidation state of copper and gold in several solvents, and to the consequent experimental difficulties.

In view of the extensive thermodynamic data available for N-donor ligands (aliphatic, cyclic, aromatic, branched, containing other donors, etc.) and for the simplest but at the same time most rational view of all data, we focused our analysis on (i) simple primary monoamines with increasing chain length in the aliphatic N-substituent, to demonstrate the role of inductive and steric effects in amine basicity and donor properties; (ii) complete sets of increasingly N-alkylated primary, secondary and tertiary acyclic monoamines in protic and aprotic solvents, to study the influence of substituent and solvent on affinity for metal(I) ions; (iii) linear polyamines (from 2 to 5 N-donor atoms) containing from 2 to 5 sp^3 N atoms, to demonstrate the influence of number of donors and their steric and electronic properties on metal(I) coordination. As regards this point, it must be emphasised that N-methylated tertiary amines stabilise the 1+ oxidation state of copper in aqueous solutions [32,42], which is of great interest for its role in biological systems [45].

Lastly, we also considered pyridine and (mixed sp^2 and sp^3) amino-pyridine ligands, in order to assess the subtle interplay between solvation, electronic and structural rigidity effects on the stability of the resulting complexes. The literature search was extended to cover most of thermodynamic data in different media, however particular discussion has been devoted to water, acetonitrile (AN) and dimethylsulfoxide (DMSO) solvents where most of the studies on the 1+ ion complexation were carried out. The data analysed here refer to the ligands shown in Scheme 1.

2. Solution properties of monovalent group 11 cations

2.1. Relative stabilities of oxidation states

Solvation of copper ions (i.e., Cu(I) and Cu(II)) changes with solvent properties to such an extent that the log of the disproportionation equilibrium $2Cu^+ \rightleftharpoons Cu^{2+} + Cu_{(s)}$, which is $\log K_D = +6$ in water, becomes 0.2 in DMSO [46,47] and is very low in pyridine (PY) ($\log K_D = -14$) [48], and AN ($\log K_D = -21$) [49] solvents, where Cu(I) has significant stability.

The distribution of 1+ and 2+ oxidation states of silver in water is very different from those of copper: $\log K_D$ for the equilibrium $2Ag^+ \rightleftharpoons Ag^{2+} + Ag_{(s)}$ in water is very low ($\log K_D = -20$) [50], so that Ag(I) is the most stable oxidation state for silver in both water and non-aqueous solvents. Ag(II) is detected in solution only when stabilised by very strong ligands, such as tetraazamacrocycles in aqueous solution [35,50].

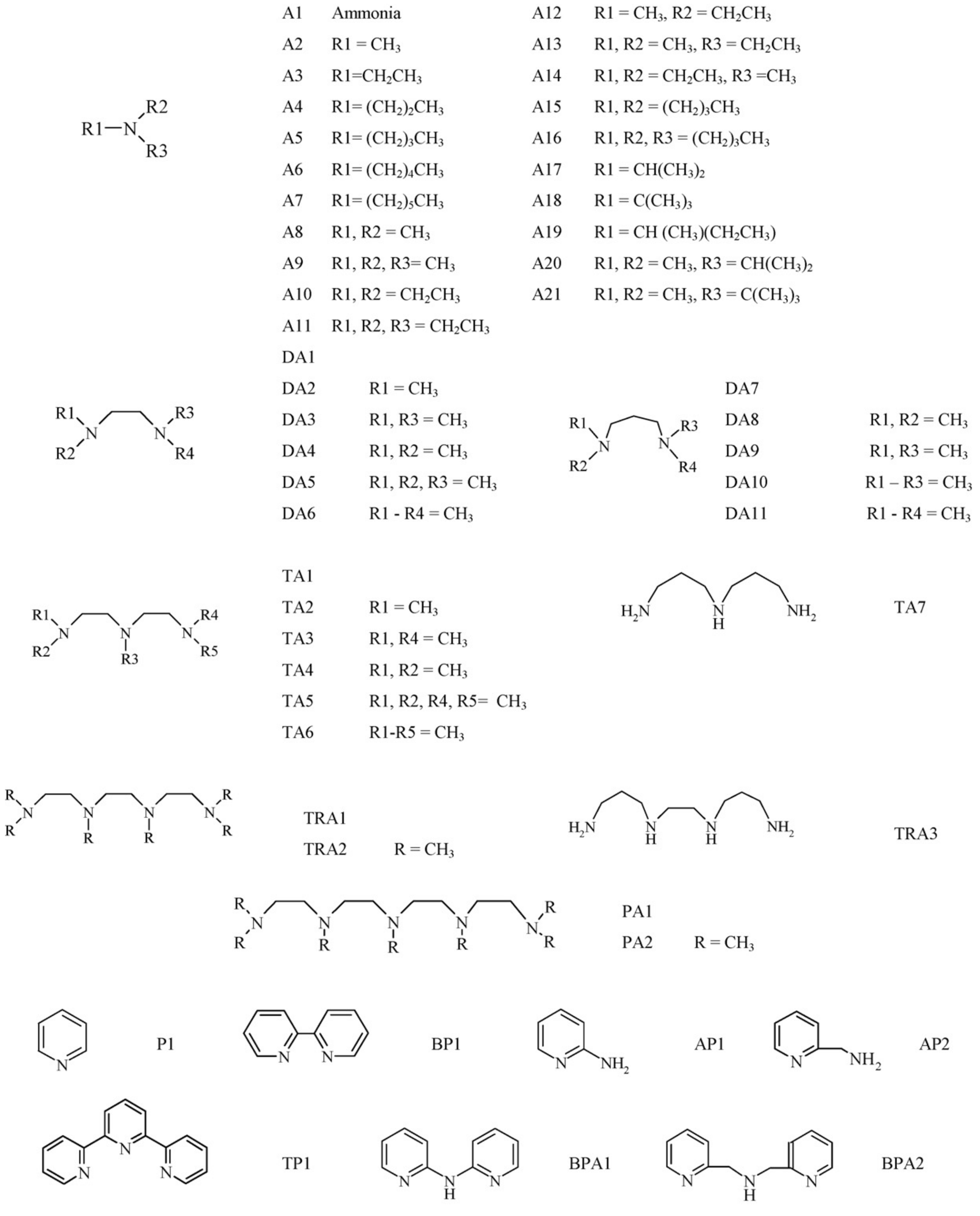
The Au(I) ion is exceptionally unstable in water, as it easily disproportionates, according to the reaction $3Au^+ \rightleftharpoons Au^{3+} + 2Au_{(s)}$ ($K = 10^{10}$ [51]). Au(I) is stable in aqueous solution only in the presence of strong stabilising ligands [51], whereas 1+ is the stable oxidation state for gold in both dimethylsulfoxide and acetonitrile [52]. A theoretical approach has recently, been proposed to estimate the stability constants of Au(I) (and also Ag(I) and Cu(I)) with ammonia in water [14].

These electrochemical features explain why most of the available data on metal(I) complexes concern Ag(I) in both aqueous and non-aqueous solvents, whereas those for Au(I) and Cu(I) are limited to non-aqueous solvents or, for Cu(I), to the very particular case of complexation by some tertiary N-alkylated polyamines (see below).

2.2. Solvation and energies of transfer

The coordination of a ligand to a metal ion in solution occurs in competition with the solvation of the species involved in the reaction. Therefore, knowledge of the properties of the various solvents is of fundamental importance, in order to interpret the effect of the medium on ligand–metal interactions.

The solvation free energy and enthalpy of an ionic compound (ΔG°_{solv}, ΔH°_{solv}) are associated with phase transfer of the crystalline solid in solution, and obviously depend on both nature of species and solvent. The solvation functions can be calculated with accuracy by measuring the free energy and enthalpy of solution of solid compounds, whereas equivalent single-ion solvation functions (ΔG°_{solv}, ΔH°_{solv}), which reflect ion–solvent interactions, cannot be determined experimentally on the basis of thermodynamic assumptions alone [53].



A1 Ammonia
A2 $R1 = CH_3$
A3 $R1=CH_2CH_3$
A4 $R1= (CH_2)_2CH_3$
A5 $R1= (CH_2)_3CH_3$
A6 $R1= (CH_2)_4CH_3$
A7 $R1= (CH_2)_5CH_3$
A8 $R1, R2 = CH_3$
A9 $R1, R2, R3= CH_3$
A10 $R1, R2 = CH_2CH_3$
A11 $R1, R2, R3 = CH_2CH_3$
A12 $R1 = CH_3, R2 = CH_2CH_3$
A13 $R1, R2 = CH_3, R3 = CH_2CH_3$
A14 $R1, R2 = CH_2CH_3, R3 =CH_3$
A15 $R1, R2 = (CH_2)_3CH_3$
A16 $R1, R2, R3 = (CH_2)_3CH_3$
A17 $R1 = CH(CH_3)_2$
A18 $R1 = C(CH_3)_3$
A19 $R1 = CH\ (CH_3)(CH_2CH_3)$
A20 $R1, R2 = CH_3, R3 = CH(CH_3)_2$
A21 $R1, R2 = CH_3, R3 = C(CH_3)_3$

DA1
DA2 $R1 = CH_3$
DA3 $R1, R3 = CH_3$
DA4 $R1, R2 = CH_3$
DA5 $R1, R2, R3 = CH_3$
DA6 $R1 - R4 = CH_3$

DA7
DA8 $R1, R2 = CH_3$
DA9 $R1, R3 = CH_3$
DA10 $R1 – R3 = CH_3$
DA11 $R1 - R4 = CH_3$

TA1
TA2 $R1 = CH_3$
TA3 $R1, R4 = CH_3$
TA4 $R1, R2 = CH_3$
TA5 $R1, R2, R4, R5= CH_3$
TA6 $R1\text{-}R5 = CH_3$

TA7

TRA1
TRA2 $R = CH_3$

TRA3

PA1
PA2 $R = CH_3$

P1 BP1 AP1 AP2

TP1 BPA1 BPA2

When not specified R = H.

Scheme 1.

In most cases, when thermodynamic functions in water are known for hydration reactions ($\Delta G^\circ_\mathrm{h}$, $\Delta H^\circ_\mathrm{h}$, $T\Delta S^\circ_\mathrm{h}$) and measurement of solution thermodynamic data is possible in a given solvent, extra-thermodynamic assumptions allow calculation of the corresponding thermodynamic changes for the transfer of single ions between water and organic solvent, $\Delta G^\circ_\mathrm{tr}$(water → solvent), $\Delta H^\circ_\mathrm{tr}$(water → solvent). Obviously, if the species are not stable in water, like Cu(I) and Au(I) ions [54,55], only solvation energies in other solvents and solvent → solvent transfer functions can be derived.

The Gibbs free energies of transfer for single ions are obtained by means of several experimental approaches (including potentiometry, polarography, and cyclic voltammetry, although in the latter two cases, equilibrium at the electrode surface

Table 1
Free energies and enthalpies of transfer, ΔG°_{tr}(AN → solvent), ΔH°_{tr}(AN → solvent), for Ag(I), Cu(I), and Au(I) ions, expressed in kJ mol^{-1}

	ε	An	Dn	Ag(I)		Cu(I)		Au(I)	
				ΔG°_{tr}	ΔH°_{tr}	ΔG°_{tr}	ΔH°_{tr}	ΔG°_{tr}	ΔH°_{tr}
Water	78.36	54.8	18	22.3[a]	41[b]	52.1[b]	–	30.9[a]	–
DMSO	46.45	19.3	29.8	−11.9[a]	−10[b]	10.6[b]	30[b]	−28.9[a]	–
PY	12.91	14.2	33.1	−34.8[a]	−66[b]	40.5[b]	55[b]	−68.5[a]	–
DMF[c]	36.71	16.0	26.6	7.4	6.0	–	–	–	–
PC[c]	64.92	18.3	15.1	45.8	51.6	–	–	–	–

AN is reference solvent. The dielectric constant (ε), donor (Dn) and acceptor (An) numbers are the taken from Ref. [153].

[a] Calculated values from Ref. [54].

[b] Calculated values from Ref. [171].

[c] Calculated values from Ref. [172].

must be established), whereas enthalpies are obtained by solution calorimetry. For experimental procedures and extra-thermodynamic assumptions applied to obtain solvation free energies and enthalpies, see Refs. [53,56].

Available transfer functions for Ag(I), Cu(I) and Au(I) from AN, considered as reference, to several common solvents are listed in Table 1. They range from protic water to aprotic organic solvents DMSO, dimethylformamide (DMF), pyridine and propylene carbonate (PC). DMSO, like water, DMF and PC, coordinate all the cations discussed *via* oxygen, and pyridine and AN coordinate cations *via* nitrogen.

For Ag(I), the complete set of Gibbs free energy data (Table 1) produces an affinity scale: PY > DMSO > AN > DMF > water > PC. For Cu(I), the order is AN > DMSO > PY > water, and for the rather soft Au(I), PY > DMSO > AN > water. These data predict a decrease in the stability of metal-amine complexes going from water to organic solvents, if only metal–ion–solvent solvation strengths are considered.

For most ions, the heats of solvation [57] are more exothermic in a strongly solvating aprotic solvent, such as DMSO, than they are in a strongly solvating protic solvent such as water. This may reflect the higher energy required to break the strong hydrogen bonds of the water structure than to disrupt the structure of liquid DMSO. The solvents coordinating *via* nitrogen can exhibit special preferences. The fairly soft donor PY shows a very high affinity for the markedly soft acceptors like Ag(I) and Au(I). While the very soft Ag(I) slightly prefers DMSO to AN, while Cu(I) markedly prefers AN to PY (Table 1).

2.3. *Solvation structures of metal(I) ions*

The structures of Cu(I) and Ag(I) ions solvated by AN show tetrahedral geometry in both solid and solution states. Tetrahedral coordination in solution has been demonstrated in AN at room temperature by EXAFS [58,59] and large-angle X-ray scattering techniques [60]. Structures in solution differ slightly from those in the solid state [61], in which both $[Cu(CH_3CN)_4]ClO_4$ and $[Ag(CH_3CN)_4]ClO_4$ are isostructural. Tetrahedral coordination of four AN molecules has also been shown for Au(I) [62]. In pyridine solvent, the perchlorate solvates of Cu(I), Ag(I) and Au(I) are tetrahedral, as proven by LAXS studies [60,62]. A regular tetrahedral configuration is found also in the solid state for Cu(I) [63] and Ag(I) [64] tetrakis(pyridine)perchlorate. The difference in M–N bond distances between Ag(I) and Au(I) is 0.06 Å in AN, but becomes 0.14 Å in PY. The Au(I) ion has a smaller ionic radius than Ag(I), due to the f-shell contribution and relativistic effects, which are especially pronounced [14,65]. The increasing difference between Ag(I) and Au(I) with increasing softness of the solvent is due to the higher polarisability of Au(I) with respect to Ag(I). The distance Cu(I)-N(solvent) is about 0.26 Å shorter than Ag(I)-N(solvent) in the same solvents, as nitrogen coordinating solvents especially favour Cu(I) [52]. EXAFS experiments demonstrate that Cu(I) in DMSO is bound to four oxygens with Cu–O distances which suffer from quite large uncertainty [60]. Recently, the geometry of $[Ag(H_2O)_4]^+$ and $[Ag(DMSO)_4]^+$ was determined in solution by LAXS and EXAFS experiments [39], showing oxygen coordination in both cases, despite the fact that soft metal ions often prefer to bind sulfoxides through sulfur [66]. DFT calculations [10], run in vacuum for $[Ag(DMSO)_4]^+$ and $[Ag(H_2O)_4]^+$, are in good agreement with experimental data, confirming the reliability of this computational approach in predicting structural parameters of complexes. Single-crystal X-ray diffraction analysis of the $[Ag(DMSO)_4]ClO_4$ adduct [39] shows that DMSO is oxygen bonded to Ag(I) in the solid state. Similarly, spectroscopic studies demonstrate distorted tetrahedral geometry for Ag(I) solvates even in the oxygen-donor solvent *N*,*N*′-dimethylpropyleneurea (DMPU) [39].

3. Factors affecting basicity of primary, secondary and tertiary amines

In the last few decades, considerable effort has been devoted to the study and rationalisation of the factors on which the basicity of organic substances depends. Starting from the early 1940s, many of these studies aimed at elucidation of the so-called "anomalous order" of the basicity scale of amines in water (i.e., NH_3 < primary < secondary < tertiary), which contrasts with the order expected if the inductive contributions of the substituents dominate (tertiary > secondary > primary > NH_3) [67–70]. This issue presented difficulties in interpretation for many years [68–71]. Great improvement in understanding of the basicity of aliphatic amines came from the first pioneering studies, and later ones on gas-phase basicity [72,73].

In 1965 [72], Munson demonstrated that the basicity of alkyl amines in the gas phase increases with the size of the alkyl groups. He found that the basicity order for primary amines was *tert*-butylamine > isopropylamine > ethylamine > methylamine; for secondary ones, diethylamine > dimethylamine; and for tertiary ones, triethylamine > trimethylamine. The inductive effect was accepted as the most reasonable explanation for these trends for many years, although Brauman's observation that alkyl groups enhance both gas-phase acidity and basicity of neutral molecules [73] demonstrated the importance of polarisability in the stabilising effect exerted by alkyl groups. As the stabilisation energy of electrostatic charge-induced dipoles is directly proportional to the ratio α/r^4 (α = polarisability; r = distance) [73], stabilisation should increase: (a) with the increase in substituent polarisability which, in turn, depends on the substituent number of atoms, bonds, etc.; (b) with the greater proximity of substituent atoms to the charged centre. Consistent with this picture, amine gas-phase basicity increases on passing from methyl to ethyl substitution, and when increasingly polarisable alkyl substituents bond to the donor atom: **A18** > **A17** > **A4** > **A3** > **A2** > **A1** [73]. Brauman also noted that the order tertiary > secondary > primary only holds if alkyl size is constant. Larger alkyl substituents may compensate for the increased degree of substitution [**A8** ≈ **A17** and **A9** ≈ **A10**] or make less substituted amines more basic [**A18** > **A17**] [73].

Once suitable explanations for the order of gas-phase basicity had been established, studies of amine basicity in solution could be undertaken on more solid thermodynamic bases.

The anomalous trend of the basicity of amines in water has been the subject of many studies, and several explanations have been proposed for it. One is the oldest B strain theory which, when proposed, gained widespread popularity [67–70]; more recent studies include competition between alkyl stabilisation (see above) and solvation effects of alkyl ammonium ions [74–76]. In this review, we think it unnecessary to analyse the subject in detail, but do think it opportune to examine briefly the main factors that the more recent studies indicate as the main agents responsible for the basicity of amines in water.

The pK_as trend for the protonation constants of substituted methylamines in water [**A1**, 9.24; **A2**, 10.64; **A8**, 10.77; **A9**, 9.76] [2] does not fit amine gas-phase basicity [**A1** ≪ **A2** ≪ **A8** ≪ **A9**] mainly due to (a) the ability of the solvent to delocalise the cation charge by hydrogen bonding; (b) the steric hindrance of amine substituents towards solvation. Ammonium, through its four hydrogens, can disperse its charge to the solvent and thus be stabilised much more than trimethylammonium, which has only one N–H. Thus, in contrast to the large difference observed in the gas phase, the basicity of trimethylamine in water is only slightly higher than that of ammonia.

The explanation of the effect of steric hindrance on solvation is quite simple. In the gas phase, the inductive effects of methyl substitution are apparent, because the ammonium ions are not solvated. In water, methyl groups sterically hinder solvation and become so important with increasing substitution that inductive effects are cancelled. In general, changing the nature of the nitrogen substituent, from methyl to larger alkyl groups, has little effect on the basicity of primary amines, because inductive effects are less important than solvation. It follows that the log K values of the protonation constants for the series **A2**–**A7** are almost the same, around 10.6 [77]. However, if the R group is changed in tertiary amines $RN(CH_3)_2$, inductive effects are observable, as the pK_a in water [78] follows the expected order: **A9** (9.76) < **A13** (9.99) < **A20** (10.30) < **A21** (10.52).

The interpretation here is that the extent of solvation of the proton in $R(CH_3)_2NH^+$ cations is so diminished by steric hindrance to solvation, due to the increase in alkyl groups along the series, that it becomes less important than the increased inductive effect. In agreement with this picture, the pK_a of trimethylamine (9.76) is lower than that of triethylamine (10.65) [78].

The basicity of amines in non-aqueous solvents has received relatively less attention than that in aqueous solution. Several disaggregate studies have been reported in DMSO [79–82], AN [79,80,82–84], pyridine [85], tetrahydrofurane [82,86,87], PC [80,88,89], tetrachloromethane [90,91], tetrachloroethylene [90,92], trifluoroethanol [93], ethanol [94,95], benzene [96], nitromethane [97], methanol [84,89,98], nitrobenzene [99–101], hexane and cyclohexane [102].

Over the years, solute–solvent interactions have aroused widespread interest and many publications have appeared on the subject; some of these are listed in Refs. [103–109]. Among publications concerning the amine basicity in particular, we suggest the excellent review by Taft [75], in which solvent effects on proton transfer equilibria of a large number of organic substances (including amines) are rationalised and quantified, and more recent papers by Headley et al. [110–113].

In the Taft paper, the trends of the basicity of 10 amines in 5 solvents (AN, water, DMSO, ethylene glycol (EG) and hexamethylphosphoramide (HMPA)) are reproduced by linear equations, in which solvent effects on proton transfer equilibria between a reference acid ($NH_4{}^+$) and the selected base (B):

$$NH^+_{4(s)} + B_{(s)} \rightleftharpoons BH^+_{(s)} + NH_{3(s)} \qquad (1)$$

are interpreted in terms of the changes in $\delta_s\Delta G^\circ$ (that is, the difference between the free energy of equilibrium (1) in the gas phase ($\Delta G^\circ_{(g)}$) and in the selected solvent ($\Delta G^\circ_{(s)}$, see Ref. [75], p. 322) with solvent dipolarity parameter π^* and solvent hydrogen bond acceptor ability β [75]. In his review, Taft states that the calculated $\delta_s\Delta G^\circ$ with the linear equation for $B = (CH_3)_3N$ agree with experimental values to within the experimental errors. "However, due to the relatively few solvent data, this correlation is not as trustworthy as is desired. Additional data in other solvents are needed to test the reliability of equation."

More recently Headley et al. [110–113] studied solvent effects on amine basicity. Their papers, which cover a larger number of amines and solvents, give quantitative analyses of both solvent and substituent effects of a series of alkyl-substituted dimethylamines [112] and propylamines [111]. Regression analysis demonstrated that both these effects mainly depend linearly on π^*, β and α. π^* and β have the same meaning as above, whereas α represents the solvent's hydrogen bond donor ability [75]. The extent and importance of the various substituents, or solute–solvent interactions, on amine basicity are given by the sign and magnitude of the coefficients of π^*, β and α in the linear equations. For all solvents studied, the size of alkyl substituents on dimethylamines plays a significant role in basicity, which increases primarily with substituent polarisability. The sensitivity of amine basicity to a change in substituent depends largely on dipolarity/polarisability (π^*) and on the basicity (β) properties of solvents. The protonation reaction of dimethylamines is sensitive to changes in both substituent group and solvent. The difference in basicity among substituted amines is larger in the less polar AN than in the more polar DMSO [112].

Improvements to this approach were recently suggested [110], based on the replacement of empirical descriptors (π^*, β and α) with a set of parameters obtained by computational methods. Good agreement is obtained between the predicted basicity values and the experimental ones of 14 substituted dimethylamines in 8 solvents and in the gas phase. The Lewis basicity (ε_B) and polarisability/dipolarity (π_I) of the solvent are important factors contributing to variations in amine basicity.

In the past 15 years, there has been considerable interest in theoretical approaches to calculate the acidity or basicity of organic compounds. Thanks to the remarkable development of computational chemistry, the acidity and basicity of organic molecules in the gas phase can now be calculated with high accuracy. Prediction of acidity and basicity in solution is much more difficult, and several theoretical approaches have been devised to meet this challenge. Among them, dielectric continuum solvation methods (DCSM) have become quite popular in recent years. In some instances, DCSM methods are unable to give accurate predictions, because they present inadequate treatment of the short-range electrostatics of polar solutes and ions and neglect hydrogen bonding. For this reason, some implementations to the method have recently been suggested. Readers interested in theoretical approaches devised to predict the acidity and basicity of organic substances in the gas phase and in solution may refer to some recent papers on the subject [114–118].

4. Thermodynamic data of Cu(I), Ag(I) and Au(I) with the N-donors

4.1. Coordination of monoamines in water

Given our aim of comparison with complexation features in aprotic solvent media, mixed protonated species, generally formed in water, are not discussed here.

Although there are no stability data on amine coordination to Au(I) in aqueous solution we just mention that theoretical calculations and gas-phase experiments predict Au(I) ion to prefer by far linear dicoordination with ammonia and phosphine [119]

On the contrary, Cu(I) and Ag(I) ions form stable complexes with ammonia and aliphatic monamines. Generally, Ag(I) and Cu(I) are able to form complexes with a variety of coordination numbers in the solid state, ranging from 2 to 4, with a preference for tetracoordination for the latter ion [51]. Coordination numbers 5 and 6 are considered less common. For Ag(I) ion, the ability to assume linear coordination geometry was classically explained in terms of the electronic structure, by the formation of two hybrid sd orbitals (from atomic 5s and $4d_{z^2}$), in which electron density is shifted from the lobes of d_{z^2} orbital to the ring [51,120,121]. This produces reduced electron density along the z-axis, which can be occupied by the lone pairs of the two ligands. However, molecular dynamics simulations [122] demonstrated that there is a distribution of coordination numbers of $[Ag(NH_3)_2(H_2O)]_n^+$ in aqueous solutions ($NH_3 \sim 10\,mol\,dm^{-3}$) with $2 < n < 4$. Also FT-ICR mass spectrometry experiments combined with DFT calculations gave a number of possible species formed by Ag(I) and NH_3 indicating that the picture of a pure linear dicoordination with ammonia in aqueous solution is a rough description [120].

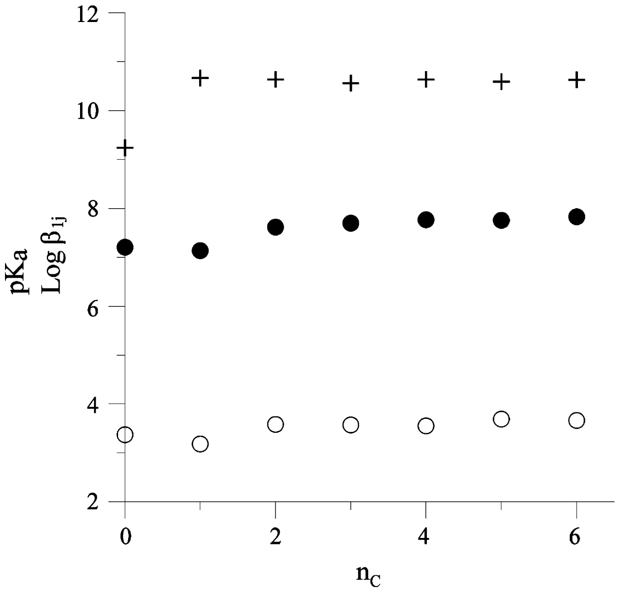


Fig. 1. pK_a for amines **A1**–**A7** in water (+) and log β_{1j} for formation of their Ag(I) complexes [(●) $j=1$; (○) $j=2$). Values from Refs. [77,123,124] (see Scheme 1 1for ligands).

The values[1] of log β_{11} and log β_{12} for the complexation of Ag(I) by primary monoamines with increasing aliphatic chain length and the pK_a of the corresponding amines are reported in Fig. 1 as a function of the number of amine carbon atoms, n_c ($n_c = 0$–6, i.e., **A1**–**A7**). Many reliable data are available both for the protonation constants of monoamines and Ag(I) complexation, also obtained at various temperatures and ionic media, so that the most homogeneous were chosen. For ammonia (**A1**), pK_a (9.24) and log β_{ij} values at $T = 298$ K (log $\beta_{11} = 3.37$, log $\beta_{12} = 7.21$) and $I = 0$ are taken from [123,124]. Data for primary amines, **A2**–**A7**, from Ref. [77], refer to $T = 298$ K in a very diluted ionic medium (the authors verified that the results were independent of ionic strength, which varied between 0.01 and $0.036\,mol\,dm^{-3}$). Their pK_a values were of negligible variance with increasing chain length of N-substituents (see Section 3) [125], whereas a slight

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[1] In this review, overall stability constants and thermodynamic functions for the reaction $iM^+ + jL \rightleftharpoons M_iL_j^{i+}$ are reported as β_{ij}, or log β_{ij}, and ΔG°_{ij}, ΔH°_{ij}, ΔS°_{ij}, respectively. Stepwise values for the mononuclear complex formation refer to the reaction $M^+ + jL \rightleftharpoons ML_j^+$ and are represented by K_j and ΔG°_j, ΔH°_j, ΔS°_j.

decrease in $\log\beta_{11}$ for the Ag(I) complexes was observed with order **A7** ∼ **A6** ∼ **A5** > **A4** ∼ **A3** > **A1** > **A2**; this also occurs for $\log\beta_{12}$. The decrease in stability constants from ammonia to methylamine (**A2**), observed despite the higher $\mathrm{p}K_\mathrm{a}$ of the latter, is probably due to the lower solvation of the corresponding **A2** complexes, as a result of the lack of hydrogen bonding between substituting methyl group and solvent. The solvational effect stabilising **A1** over **A2** complexes may be compensated by the inductive effect in **A3**–**A7**. Evidently, this effect decreases with chain lengthening, as $\log\beta_{1j}$ values for **A5**–**A7** are nearly equal. The ΔH°_{12} values available for Ag(I) complexation with **A2**–**A7** are ascribed to electrostatic effects [77], but the absence of reliable values for ΔH°_{11} does not allow a detailed thermodynamic description. The values of $\log\beta_{11}$ and $\log\beta_{12}$ for the formation of Ag(I) complexes with bulky primary monoamines, such as **A17**–**A19** [125] (not plotted), are in line with this observation.

Hancock [125] suggested that the different trends of $\mathrm{p}K_\mathrm{a}$ and $\log\beta_{ij}$ in water are due to the lower influence of steric hindrance of amines for Ag(I) with respect to the proton complexation. However, this conclusion was not confirmed by other experimental evidence, and contrasts with the small difference between the enthalpies of protonation, $\Delta H^\circ_\mathrm{p}$, of **A6** and **A2** ($\Delta\Delta H^\circ_\mathrm{p} = \Delta H^\circ_\mathrm{p}(\mathbf{A6}) - \Delta H^\circ_\mathrm{p}(\mathbf{A2}) = -2.9\,\mathrm{kJ\,mol^{-1}}$ [126]), which is very close to that between the available [77] enthalpies of formation of $\mathrm{AgL_2}$ complexes with the same amines ($\Delta\Delta H^\circ_{12} = \Delta H^\circ_{12}(\mathbf{A6}) - \Delta H^\circ_{12}(\mathbf{A2}) = -2.6\,\mathrm{kJ\,mol^{-1}}$).

Furthermore, from Refs. [126,77] it seems that protonation and complexation constants are the result of different phenomena: it can be seen that while the $\log\beta$ values depend on the ΔH°_{12} values (similar ΔS°_{12} for all the reactions), the nearly constant $\mathrm{p}K_\mathrm{a}$ of **A2**–**A7** are the result of an entropy–enthalpy compensation, rather marked for **A2** and **A3**. To this respect, the determinations of accurate ΔH°_{11} values would be helpful.

Homogeneous stability constants (at 303 K and $I = 0.5\,\mathrm{M}$) are available in water only for $[\mathrm{CuL_2}]^+$ formation with L = **A1**, **A2** and **A3**. The $\log\beta_{12}$ values, obtained by the polarographic method, are 10.4 and 10.1 for **A1** and **A3**, respectively [127], whereas $\log\beta_{12}$ values of 9.21 and 9.62 were found for **A2** by the polarographic-redox potential/half-wave potential method in $2\,\mathrm{mol\,dm^{-3}}$ ionic medium [128]. The values are always higher for Cu(I) than for Ag(I) complexation.

The data reported in Fig. 1 for ammonia are in good agreement with those at 291 K given earlier by Bjerrum et al. [129] ($\log\beta_{12} = 10.86$, $\Delta H^\circ_{12} = -66.9\,\mathrm{kJ\,mol^{-1}}$), who also found $\log\beta_{11} = 5.93$ for $[\mathrm{Cu(NH_3)}]^+$ formation by potentiometry (Cu/Hg electrode). In addition, a quite high value of $\log\beta_{12} = 11.38$ for the formation of the $[\mathrm{Cu(NH_3)_2}]^+$ complex was also proposed, as a result of study of the ternary system $\mathrm{Cu(I)/NH_3/Cl^-}$ [130]. More recently, Bjerrum, in a higher ammonia concentration, also found $\log K_3$ for $[\mathrm{Cu(NH_3)_3}]^+$ and $[\mathrm{Ag(NH_3)_3}]^+$ complex formation ($T = 298\,\mathrm{K}$; $\log K_3 = -1.26$ and -1.60 for Cu(I) and Ag(I), respectively) [131], which follows the same trend as β_{12}, that is, Ag(I) < Cu(I).

A value of $\log\beta_{12} = 26.5$ has only been estimated for Au(I)-**A1** complexation [132], and a $\log K_1 = 9.8$ has recently been estimated by DFT [14]. The latter was considered reasonable by the above authors in relation to the $\log K_1$ values for metal ions close to Au in the periodic table ($\log K_1(\mathrm{Hg(NH_3)^{2+}}) = 8.8$) [14].

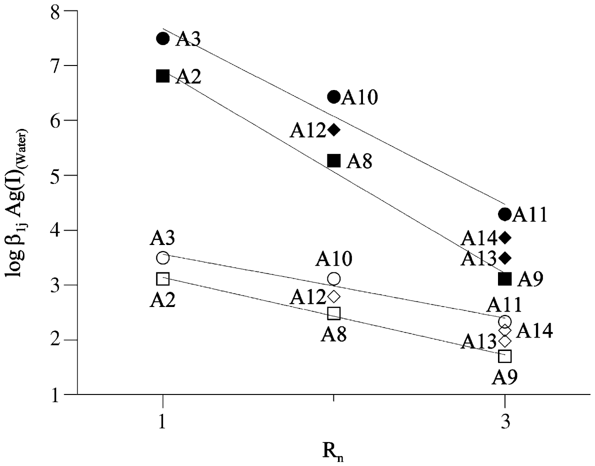

Fig. 2. $\log\beta_{ij}$ for Ag(I) complexation vs. R_n, number of alkyl substituents on amine group ($\log\beta_{11}$, empty symbols, $\log\beta_{12}$ full symbols). Values from Refs. [134,135].

The data for the formation of Ag(I)-amine complexes are rather unusual, because the stability constant for the formation of the first 1:1 complex (K_1) is often lower than K_2. A recent paper [133] studied this trend by means of DFT and also examined solvent effects, in order to interpret the $\log\beta_2$ of Ag(I) complexes much lower than those for Cu(I) and Au(I). The paper demonstrated that the low stability of the first aquo complex of Ag(I) with ammonia, $[\mathrm{Ag(NH_3)(H_2O)}]^+$, favours binding of the second molecule of $\mathrm{NH_3}$ and the observed stability order is $K_1 < K_2$. These results are in line with the lower binding ability of Cu(I), Ag(I) and Au(I) with water than for ammonia, and may also be used to explain the similar behaviour of monoamines in water. The above authors [133] state that the same may occur with Cu(I), but nothing is anticipated for Au(I).

Fig. 2 shows the $\log\beta_{1j}$ ($j = 1$, 2) of Ag(I) complexation versus R_n, the number of N-alkyl substituents for similar families of monoamines, methylated **A2**, **A8**, **A9** (squares) and ethylated **A3**, **A10**, **A11** (circles), chosen in order to demonstrate the influence of increasing N-alkylation on affinity for Ag(I) in water. The data refer to 298 K and $I = 1\,\mathrm{mol\,dm^{-3}}$ [134], apart from the available β_{12} for Ag(I)-**A9** referring to 288 K and $I = 0.1\,\mathrm{mol\,dm^{-3}}$ [135]. The data for **A2** and **A3** are in excellent agreement with those at $I = 0.1\,\mathrm{mol\,dm^{-3}}$ [125], $I = 0.0\,\mathrm{mol\,dm^{-3}}$ [77] and $I = 0.5\,\mathrm{mol\,dm^{-3}}$ [136]. There is a clearcut decrease in the stability constants going from primary amine (**A2**, **A3**) to secondary amine (**A8**, **A10**) and tertiary amine (**A9**, **A11**). This has been explained by some authors [137] as due to (i) a decrease in the basicity of amino groups in the order $-\mathrm{NH_2} > -\mathrm{NHR} > -\mathrm{NR_2}$; (ii) elongation of M–N bonds, due to steric strain; (iii) decreased solvation of the complexes, as a consequence both of their increased radii and of the lesser extent of hydrogen bonding brought about by the N-alkylated amines.

For the same reasons, an inversion in the trends of $\log K_1$ and $\log K_2$ (that is, $K_1 > K_2$) is observed going from secondary

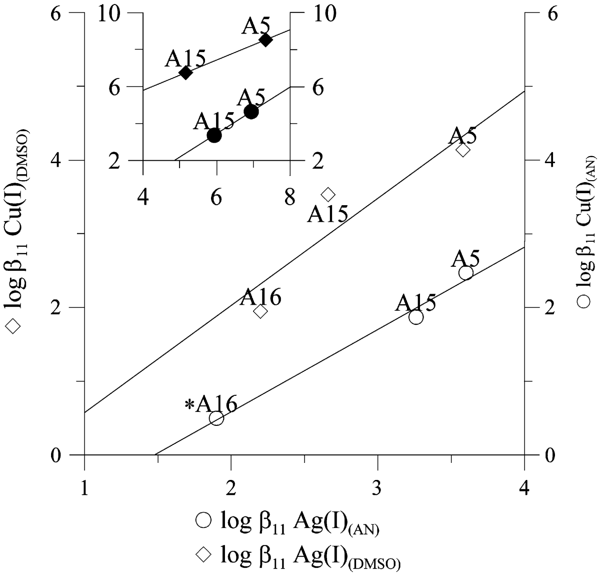

Fig. 3. log β_{11} Cu(I) vs. log β_{11} Ag(I) of complexes of primary amine (**A5**), secondary amine (**A15**) and tertiary amine (**A16**) in AN (◯) and DMSO (◇); in frame, log β_{12} Cu(I) (y-axis) vs. log β_{12} Ag(I) in AN (●) and DMSO (♦). (*log β_{11} Cu(**A16**)$^+$ in AN < 0.5) Values from Refs. [12,27].

to tertiary amines. Every replacement of a methyl by an ethyl group (see also data of Fig. 2 (diamonds) for **A12**–**A14** mixed methyl–ethyl N-substituted ligands) increases global as well as stepwise formation constants. This suggests that the extra inductive effect of an ethyl group is more important for complexation than the increase in steric strain. The slopes of the lines fitting log β_{12} values for the methyl- and ethyl-substituted families are similar, and higher than those of the lines fitting log β_{11} values—that is, the decrease in log β_{1j} values is much more marked, due to additional steric hindrance, for the second complex.

4.2. *Coordination of monoamines in aprotic solvents*

Only one set of stability constants is available for the coordination of increasingly N-alkylated monoamines **A5**, **A15** and **A16** (alkyl group = n-butyl) towards both Ag(I) and Cu(I) in aprotic solvents AN and DMSO [12,27]. Fig. 3 shows them in the form log β_{11} Cu(I) versus log β_{11} Ag(I) in these solvents (in the frame plot for log β_{12}). Literature data show a decrease in complex stability going from primary to secondary and tertiary n-butyl amines, in agreement with the common observation that the coordination ability of the nitrogen atoms of alkyl amines is reduced with increasing N-alkyl substitution [43], in both protic and aprotic solvents. Cu(I) complexes are more stable in DMSO than in AN, whereas Ag(I) complexes are not particularly dependent on the solvent. Literature data, generally related to Ag(I) complexes [2] with primary and secondary aliphatic monoamines in aqueous and polar non-aqueous solvents, show that they can form only [AgL]$^+$ and [AgL$_2$]$^+$ species, the Ag(I) ion being unable to bind firmly more than two monodentate ligands. The same applies to non-aromatic cyclic secondary amines such as piperidine and morpholine. The coordination stoichiometry of tertiary aliphatic amines does not show such uniform behaviour. Many non-aromatic monocyclic and bicyclic tertiary amines, such as alkyl derivatives of piperidine [2], quinuclidine [2,42] and tetraethylenediamine [42] (considered as a monodentate ligand), also form mono- and diamine complexes with Ag(I) in polar, protic and aprotic solvents. However, monodentate triethylamine (**A11**) and tri-n-butylamine (**A16**) only form 1:1 complexes with Ag(I) in DMSO [138], due to steric hindrance, which causes failure of the correlation between the basicity of the amines and the stability of the silver complexes. In a comparative study with its bicyclic analogue quinuclidine [139], triethylamine was considered as a hindered amine, because one of the three ethyl groups interferes with the region normally assigned to the unshared electron pair of nitrogen. A similar explanation has been proposed [12] for the lack of 1:2 complexes between Cu(I) or Ag(I) and **A16** in AN and DMSO. The importance of steric factors in these complexation reactions is emphasised by the large stability constants of 1:2 complexes of Ag(I) with not sterically hindered quinuclidine (log $\beta_{11} = 2.1$, log $\beta_{12} = 3.7$) and triethylenediamine (log $\beta_{11} = 2.1$, log $\beta_{12} = 3.6$) in DMSO [34]. Solvation effects play an additional role and a compromise is always reached: for example, in water triethylamine, dimethylethylamine and diethylmethylamine (**A11**, **A13** and **A14** in Fig. 2) are still able to form a second complex [134], but no data are available for the coordination of the more hindered tripropylamine and tri(n-butyl)amine **A16**. Conversely, **A16** has been proven to form two complexes [log $\beta_1 = 2.22$, log $\beta_{12} = 3.82$] with Ag(I) in 50% mole fraction EtOH–water at 25 °C [140].

Copper(I) and silver(I) interact preferentially with Lewis bases, such as AN and DMSO and less with water as already mentioned [57]. As reported in Section 2.2 and Table 1, the two cations show specific differences when their solvation is compared. Thus, the ΔG_{tr} of transfer AN → DMSO for the cations differ by 22 kJ mol^{-1}, Cu(I) being strongly favoured in AN over Ag(I), which interacts more strongly with DMSO, even with respect to water (for Ag(I), $\Delta G_{\mathrm{tr}}(\mathrm{water} \rightarrow \mathrm{DMSO}) = -34.2\,\mathrm{kJ\,mol^{-1}}$) [54].

As mentioned above, the stability constants of **A5**, **A15** and **A16** complexes of Ag(I) in AN and DMSO are comparable (see Fig. 3), despite the stronger solvation of Ag(I) in DMSO. In addition, with **A5**, Ag(I) in water also forms complexes with stability similar to those found in AN and DMSO (the values, first reported by Bjerrum [136] and later confirmed by Garner et al. [134], although at slightly different ionic strength, are log $\beta_{11} = 3.43$ and log $\beta_{12} = 7.48$).

The values log $\beta_{1\,\mathrm{water}} <$ log $\beta_{1\,\mathrm{DMSO}}$ – which are unexpected, considering the unfavourable free energy of transfer of Ag(I) from water to DMSO – may be explained by the greater solvation of the ligand in water, *via* hydrogen bonds, which evidently compensates for the lower solvation of silver ion in this solvent. Ligand solvation, greater in water than in DMSO, was invoked to explain the complexation trends in the two solvents of primary and secondary mono or polyamines [81,112,141,142].

This effect also appears with polyamines. The expected trend, $\log \beta_{11\,\mathrm{water}} > \log \beta_{11\,\mathrm{DMSO}}$, for both Ag(I) and other transition metal complexes [8,9,26], is re-established with ligands unable to from hydrogen bonds in water, like pyridines [10] or tertiary amines. In this case, the higher solvation of the metal ion in DMSO prevails in governing stability.

The difference $\Delta\Delta G_{\mathrm{tr}} = \Delta G_{\mathrm{tr}}([\mathrm{AgL}_j]^+) - \Delta G_{\mathrm{tr}}(j\mathrm{L})$ between the free energy of transfer AN → DMSO of the complexes of Ag(I) with **A5** and those of free ligand/s are −11.9 and −14.5 kJ mol^{-1} when $j = 1$ and 2, respectively [12]. This means that Ag(I) in these complexes is not shielded from interactions with the solvent which, like those for the uncomplexed cation, are stronger in DMSO than in AN [12].

The difference between the free energy of transfer AN → DMSO of the 1:1 complex of Cu(I) with **A5** and that of free ligand $(\Delta G_{\mathrm{tr}}([\mathrm{CuL}]^+) - \Delta G_{\mathrm{tr}}(\mathrm{L}))$ is positive (+1.1 kJ mol^{-1}), although relatively small. This was attributed to residual solvation of Cu(I) in the complex[12]. The positive sign is in agreement with the stronger solvation of Cu(I) by AN, and accounts for the lower stability of monoamine complexes in AN than in DMSO.

Ag(I) complexes have been found to be more stable than the corresponding Cu(I) complexes in AN, whereas the opposite occurs in DMSO [12]. Basically, these results are explained by taking into account solvent competition for Ag(I) and Cu(I), as demonstrated by transfer functions (Table 1).

In the case of **A5** and **A15**, enthalpy and entropy values are available for Ag(I) in DMSO [27] and for **A5** in water [77] ($\Delta H^\circ_{11\,\mathrm{DMSO}} = -31.40$ and -31.80 kJ mol^{-1}, $\Delta S^\circ_{11\,\mathrm{DMSO}} = -37.2$ and -56 J mol^{-1} K^{-1}, $\Delta H^\circ_{12\,\mathrm{DMSO}} = -71.50$ and -61.60 kJ mol^{-1}, $\Delta S^\circ_{12\,\mathrm{DMSO}} = -99.6$ and -107.5 J mol^{-1} K^{-1} for **A5** and **A15**, respectively; $\Delta H^\circ_{11\,\mathrm{water}} = (-17)$ kJ mol^{-1}, $\Delta S^\circ_{11\,\mathrm{water}} = (+8)$ J mol^{-1} K^{-1}, $\Delta H^\circ_{12\,\mathrm{water}} = -52.70$ kJ mol^{-1}, $\Delta S^\circ_{12\,\mathrm{water}} = -16.7$ J mol^{-1} K^{-1} for **A5**. Values in brackets, i.e., $\Delta H^\circ_{11\,\mathrm{water}}$ and $\Delta S^\circ_{11\,\mathrm{water}}$, are uncertain).

A common feature of complexation reactions in water and DMSO is that complex formation is enthalpy-stabilised in both solvents, entropy term always being negative with the exception of the first complexation step for **A5** in water. This is characteristic for the formation of metal–ligand covalent bonds and results from the relatively weak solvation of neutral species involved in complex formation and the absence of charge neutralisation [52].

The first stepwise stability constant for the formation of Ag(I) complexes with *n*-butylamine (**A5**), K_1, is lower than K_2, in both water and DMSO. This trend also occurs for the complexation reactions of aliphatic primary monoamines (Fig. 2). In this case the complete set of thermodynamic functions reveals that the stability trend results from a balance between the favourable enthalpy of reaction and unfavourable entropy. In particular, the stepwise enthalpy $(-\Delta H^\circ_2 > -\Delta H^\circ_1)$ and entropy $(-\Delta S^\circ_{K_2} > -\Delta S^\circ_{K_1})$ trends can be interpreted as reflecting the greater desolvation occurring at the first step of complexation, which makes ΔH°_{11} less exothermic than ΔH°_{12}, in spite of the certainly greater metal–ligand interaction in the first complexation step [27].

4.3. Formation of polyamine complexes in different solvents

4.3.1. Diamines

Many studies have focused on the reactions of monovalent ions with unmethylated and N-methylated diamines in both water and DMSO, most of them concerning Ag(I) complexation (Scheme 1; Tables 2 and 3). Diamines **DA1**–**DA6** [143–146] can form five-membered chelate rings, **DA7**–**DA11** [24,29,147,148] six-membered rings. For the complexation reactions of Ag(I) with **DA2**, **DA5**, **DA9** and **DA10**, only data in water are available, while comparisons with DMSO are possible for other amines. Many stability data are available for the complexation of Ag(I) by **DA1** in water: the values of Table 2 at $I = 0.1$ mol dm^{-3} [143] are very close to those found in various ionic media [144,145,149].

Generally, as noted for monoamine complexation in water and DMSO, a systematic decrease in the stability constants of metal(I)-polyamine complexes occurs with increasing N-substitution for the formation of all mono- and dinuclear species.

Literature data regarding the complexation reactions of Cu(I) with diamines are very scarce and limited to **DA1**. The $\log \beta_2$ values measured in water for the Cu(I)-**DA1** system are 10.63 (303 K, $I = 2$ mol dm^{-3}) [150], 10.8 (298 K, I = unknown) [151] and 11.4 (298 K, $I = 0.3$ mol dm^{-3}) [152], showing a higher affinity with respect to Ag(I) and the absence of polynuclear species.

Tables 3–5 show that Ag(I) does form polynuclear species in both water and DMSO. The formation of the highly stable dimer $[\mathrm{Ag_2L_2}]^{2+}$ in water may be the reason for the undetectability of the mononuclear complex $[\mathrm{AgL}]^+$ in some cases [145]. The presence of one tertiary function in the ligand does not favour dimer formation, as indicated by the progressively lower $\log \beta_{22}$ values for **DA4** and **DA5** and the absence of $\mathrm{Ag_2L_2}$ for **DA6**. The binuclear species of propylene diamine is more stable than that of ethylenediamine. If dinuclear complexes $\mathrm{Ag_2L_2}$ are assumed to have cyclic structure, a 12-membered ring in the propylene diamine complex should favour the linear N–Ag–N configuration more than the 10-membered one, characteristic of ethylenediamine. Moreover, the greater distance between the donor atoms in propylene diamine complex may also make $\mathrm{Ag^+}$–$\mathrm{Ag^+}$ repulsion less important in this complex [145].

The value of ΔH°_{11}, available in water only for **DA1**, is very close to that in DMSO, in which chelation has been proposed [29]. In addition, the values of β_{11} in water, compared with those of monoamines **A1** and **A2**, fit bidentate behaviour for both **DA1** and **DA7**. For the other diamines, it is difficult to make any hypothesis, in the absence of enthalpy and entropy values.

The formation of dinuclear complexes is common to almost all polyamines in water (Table 2). In DMSO, only ligands having adjacent but not tertiary N atoms separated by more than two methylene groups, i.e., **DA7** (but also triamine **TA7** and tetraamine **TRA3**) can do this. The different speciation in aqueous and non-aqueous solutions has been explained [4] by considering the dielectric constant of the solvents ($\varepsilon = 78.5$ and 46.5 for water and DMSO, respectively) [153], which favours the formation of polynuclear species in water.

Table 2
Stability constants for reaction: $i\mathrm{Ag}^+ + j\mathrm{L} \rightleftharpoons \mathrm{Ag}_i\mathrm{L}_j{}^{i+}$ in water

Ligand	Complex	log β_{ij}
DA1	AgL[a]	5.32
	AgL_2[a]	7.62
	Ag_2L_2[b]	13.15
DA2[c]	AgL	–
	AgL_2	7.30
	Ag_2L_2	12.05
DA3[d]	AgL	3.49
	AgL_2	6.53
	Ag_2L_2	10.52
DA4[d]	AgL	3.74
	AgL_2	7.15
	Ag_2L_2	9.74
DA5[d]	AgL	3.22
	AgL_2	6.14
	Ag_2L_2	8.29
DA6[d]	AgL	2.97
	AgL_2	5.48
DA7	AgL[e]	5.85
	AgL_2[e]	7.81
	Ag_2L[f]	6.45
	Ag_2L_2[f]	14.86
DA8[f]	AgL	3.55
	AgL_2	7.11
	Ag_2L_2	11.02
DA9[f]	AgL	–
	AgL_2	6.27
	Ag_2L_2	12.12
DA10[f]	AgL	2.91
	AgL_2	5.52
	Ag_2L_2	9.61
DA11[f]	AgL	2.21
TA1	AgL[g]	6.1
	Ag_2L[g]	7.5
	AgL_2[h]	7.90
	Ag_2L_2[h]	15.1
	Ag_3L_2[h]	17.94
TA2[h]	AgL	–
	AgL_2	7.87
	Ag_2L_2	14.4
	Ag_3L_2	16.74
TA4[h]	AgL	–
	AgL_2	7.74
	Ag_2L_2	13.84
	Ag_3L_2	15.35
TA5[h]	AgL	4.14
	AgL_2	7.74
	Ag_2L_2	10.89
	Ag_3L_2	12.35
TRA1[i]	AgL	7.7
	Ag_2L	10.1
P1[j]	AgL	2.00
	AgL_2	4.11
BP1[k]	AgL	3.84
	AgL_2	7.37
AP1[l]	AgL	2.32
	AgL_2	4.80
AP2[m]	AgL	4.11
TP1[n]	AgL	5.79
	AgL_2	9.68
BPA2[o]	AgL	5.46
	AgL_2	8.16

$T = 298$ K and $I = 0.1$ mol dm^{-3}, unless otherwise specified in the footnote.

[a] Ref. [143], $\Delta H_1^\circ = -55.5$ kJ mol^{-1}.

[b] Ref. [144], $I = 0.5$ mol dm^{-3}, $\Delta H_{22}^\circ = -97.1$ kJ mol^{-1}.

[c] Ref. [146].

[d] Ref. [145], $I = 1$ mol dm^{-3}.

[e] Ref. [147], $T = 293$ K.

[f] Ref. [148], $I = 1$ mol dm^{-3}.

[g] Ref. [173], $T = 293$ K.

[h] Ref. [174], $I = 1.30$ mol dm^{-3}.

[i] Ref. [175].

[j] Ref. [163], $I = 0.5$ mol dm^{-3}, $\Delta H_{12}^\circ = -20.2$ kJ mol^{-1}, $\Delta H_{12}^\circ = -47.4$ kJ mol^{-1}.

[k] Ref. [166], $T = 293$ K, $\Delta H_{11}^\circ = -32$ kJ mol^{-1}, $\Delta H_{12}^\circ = -49$ kJ mol^{-1}.

[l] Ref. [176], $I = 0.5$ mol dm^{-3}.

[m] Ref. [177], $T = 293$ K.

[n] Ref. [178].

[o] Ref. [179], $T = 293$ K.

Lower stability in water than in DMSO is generally also found for the common species formed by amines containing primary and secondary amino groups, as a result of the greater solvation of amines in water [154].

The values for **DA7** [147,148] in Table 2 do not refer to the paper by Ohtaki [155], carried out in a high molar strength (3.0 mol dm^{-3}, $T = 298$ K), as in this case the stability constants seem too high in comparison also with those reported by Bertsch et al. [156] (Ohtaki data, log $\beta_{11} = 6.9$, log $\beta_{22} = 15.90$, log $\beta_{12} = 9.8$, this last given as uncertain by the authors; Bertsch values: log $\beta_{11} = 5.92$ at 293 K, log $\beta_{11} = 5.56$ at 303 K).

Both stability constants and thermodynamic functions for the complexation reactions of Ag(I) with N-substituted ethylenediamines (**DA1**, **DA3**, **DA4** and **DA6**) indicate that the ligands behave as bidentates in DMSO [24]. The data of Seeber and Zanello [157] for the systems Ag(I)-**DA1**, -**DA3**, -**DA7** and -**TRA1**, obtained at 298 K by voltammetry in DMSO, seem to be underestimated (log $\beta_{11} = 3.30$, 2.0, 2.0 and 5.32, respectively) also with respect to the data of Pool and Sandberg [158] for **DA1** (log $\beta_{11} = 6.27$, log $\beta_{12} = 9.54$, log $\beta_{21} = 5.8$).

Thermodynamic parameters (Table 3) show that the 1:1 complex of Ag(I) with **DA3** is more stable in DMSO than **DA4**. Analysis of data clarify that the less unfavourable entropy term causes higher stability, as the enthalpy terms are close to each other. This indicates that substitution of two secondary nitrogen atoms of the ethylenediamine with one primary and one tertiary do not give rise to great differences in the average M–N bond strength, whereas the asymmetric N-methylation of ethylenediamine in **DA4** does influence the first step of complexation from the entropic point of view. The authors [24] hypothesised that the solvent interacts better with symmetrical –NHR groups,

Table 3
Overall stability constants and thermodynamic functions for reaction $i\text{Ag}^+ + j\text{L} \rightleftharpoons \text{Ag}_i\text{L}_j^{\,i+}$ in DMSO at 298 K and $I = 0.1$ mol dm^{-3} (L = diamine)

Ligand	Complex	$\log \beta_{ij}$	$-\Delta G^\circ_{ij}$ (kJ mol^{-1})	$-\Delta H^\circ_{ij}$ (kJ mol^{-1})	$-\Delta S^\circ_{ij}$ (J mol^{-1} K^{-1})
DA1[a]	AgL	5.34	30.5	63	109
	AgL_2	9.50	54.2	85	103
DA3[a]	AgL	4.31	24.6	43.7	64
	AgL_2	8.31	47.4	79.3	107
DA4[b]	AgL	4.75	27.1	42.1	50
	AgL_2	8.86	50.6	86.5	120
DA6[a]	AgL	3.25	18.6	30.8	41
	AgL_2	6.24	35.6	69.3	113
DA7[b]	AgL	5.9	34	80.8	157
	Ag_2L	8.06	46.0	71.6	86
	Ag_2L_2	14.4	82	146.8	217
DA8[c]	AgL	3.95	22.5	40.9	62
	AgL_2	7.49	42.7	73.4	103
DA11[c]	AgL	1.67	9.5	21.7	41
	AgL_2	2.83	16.1	39.6	79

[a] Ref. [7].
[b] Ref. [29].
[c] Ref. [24].

forming less crowded solvates, which is not the case in **DA4** complexes. The thermodynamics of the second complexation step in Ag(I)-**DA1**, -**DA3**, -**DA4** and -**DA6** systems has also been interpreted as indicating that the ligands behave as bidentates in AgL_2 complexes [24].

The thermodynamic data of **DA8** are somewhat ambiguous in indicating the ligand coordination mode. Comparisons have been made between monoamines [27] and **DA7** [4] in DMSO: thermodynamic parameters and NMR spectroscopy [24] show that **DA8** is chelated. Symmetric dimethylation of **DA8** reverses

Table 4
Overall stability constants and thermodynamic functions for reaction $i\text{Ag}^+ + j\text{L} \rightleftharpoons \text{Ag}_i\text{L}_j^{\,i+}$ in DMSO at 298 K and $I = 0.1$ mol dm^{-3} (L = tri-, tetra- or pentaamine)

Ligand	Complex	$\log \beta_{ij}$	$-\Delta G^\circ_{ij}$ (kJ mol^{-1})	$-\Delta H^\circ_{ij}$ (kJ mol^{-1})	$-\Delta S^\circ_{ij}$ (J mol^{-1} K^{-1})
TA1[a,b]	AgL	7.46	42.6	78.2	119.5
	AgL_2	10.2	58.2	94	120
TA3[c]	AgL	6.42	36.6	64.5	94
	AgL_2	9.31	53.1	98.0	150
TA6[c]	AgL	5.44	31.0	54.5	79
	AgL_2	6.97	39.8	81.5	140
TA7[b]	AgL	7.08	40.4	68.3	94
	Ag_2L	9.98	56.9	99.2	142
	Ag_3L_2	20.64	117.8	216.2	330
TRA1[d]	AgL	10.32	58.91	91.5	109
TRA2[e]	AgL	7.82	44.6	69.3	82.8
TRA3[d]	AgL	7.93	45.25	77	106
	AgL_2	9.72	55.47	88	109
	Ag_2L	11.20	63.92	114	168
	Ag_2L_2	17.66	100.8	162	205
	Ag_3L_2	22.90	130.7	224	312
PA1[f]	AgL	10.45	59.6	87.5	94
	Ag_2L	13.71	78.2	120.1	140
	Ag_3L_2	26.4	150.7	245	316

[a] Ref. [28].
[b] Ref. [29].
[c] Ref. [7].
[d] Ref. [4].
[e] Ref. [9].
[f] Ref. [20].

Table 5
Overall stability constants and thermodynamic functions for reaction $i\mathrm{Ag}^+ + j\mathrm{L} \rightleftharpoons \mathrm{Ag}_i\mathrm{L}_j{}^{i+}$ in DMSO at 298 K and $I = 0.1\ \mathrm{mol\ dm^{-3}}$ (L = pyridine-containing ligand)

Ligand	Complex	$\log \beta_{ij}$	$-\Delta G^\circ_{ij}$ (kJ mol^{-1})	$-\Delta H^\circ_{ij}$ (kJ mol^{-1})	$-\Delta S^\circ_{ij}$ (J mol^{-1} K^{-1})
P1[a]	AgL	1.41	8.05	13.9	19.7
	$\mathrm{AgL_2}$	2.11	12.0	27.0	97
BP1[b]	AgL	2.08	11.9	20.2	27.8
	$\mathrm{AgL_2}$	3.65	20.8	41.3	68.8
AP2[b]	AgL	3.88	22.1	33.3	37.5
	$\mathrm{AgL_2}$	7.63	43.5	73.5	100.6
	$\mathrm{AgL_3}$	9.19	52.4	101	164
TP1[b]	AgL	3.03	17.3	26.6	31.1
	$\mathrm{AgL_2}$	4.68	26.7	50	78
BPA2[b]	AgL	4.37	24.9	37.7	42.9
	$\mathrm{AgL_2}$	7.30	41.6	64.2	75.8
	$\mathrm{Ag_2L_2}$	10.28	58.7	93	118

[a] Ref. [27].
[b] Ref. [10].

the peculiar feature of Ag(I), to give more stable six-membered chelate rings complexes with respect to five-membered chelate ones [24,159], strongly influencing the ligand affinity. In the case of the totally methylated **DA11**, the low basicity of the tertiary amino groups and the steric requirements of the ligand are of major importance, and chelation is prevented [24].

4.3.2. Tri-, tetra- and pentaamines

The general considerations for the complexation of Ag(I) with these amines, in water and DMSO, are similar to those given for diamines. That is (a) a decrease in the stability of the common species is observed on increasing the number of N-substituted groups in the polyamine; (b) polynuclear species (dimers) form preferentially in water rather than in DMSO.

Reaction thermodynamic parameters in DMSO show that triamines **TA1** [28,29], **TA3** and **TA6** [7] behave as tridentates, forming two 5-membered chelate rings in 1:1 silver complexes, and this probably also occurs in water. However, triamines may also behave as bidentates, forming $\mathrm{AgL_2}$ species in the Ag(I)-**TA1** [28,29] and Ag(I)-**TA3** systems [7], or as monodentate in the 1:2 Ag(I) complex of the bulky, fully substituted **TA6** [7].

The increased complexity of ligands may also favour the formation of multinuclear complexes like $[\mathrm{Ag_3}(\mathbf{TA7})_2]^{3+}$, in which three silver atoms are suggested to be linearly and simultaneously bound by two nitrogen atoms belonging to two different ligand molecules. The Ag(I)-**TA7** system has also been studied by polarography in water, in which only the complex $[\mathrm{Ag_2}(\mathbf{TA7})_2]^{2+}$ with $\log \beta_{22} = 8.59$ was detected [160].

Complexation of Ag(I) by **TA1** was studied in DMF: $\log \beta_{11} = 10.2$, $-\Delta H^\circ_{11} = 90.4$, $-T\Delta S^\circ_{11} = 32.1\ \mathrm{kJ\ mol^{-1}}$; $\log \beta_{12} = 13.18$, $-\Delta H^\circ_{12} = 108.8$, $-T\Delta S^\circ_{12} = 33.6\ \mathrm{kJ\ mol^{-1}}$ [161]. The thermodynamic data for the formation of the 1:1 complex indicate retention of the tetrahedral structure by Ag(I), even after first ligand coordination, and the formation of two fused five-membered chelate rings. The higher stability of the complexes in DMF with respect to DMSO is mainly due to the weaker solvation of the metal ion in the former solvent (see Table 1).

The stability order for the complexation reactions of Ag(I) by tetraamines in DMSO is **TRA1** > **TRA3** > **TRA2** (Table 4) and depends on the number of N-methyl substituents and on the carbon chain length between the nitrogen atoms [4,9]. **TRA3** involves formation of one 5- and two 6-membered chelate rings, forced into tetrahedral configuration: in this geometry, 5-membered chelate rings are favoured over larger ones.

To achieve chelation, adjacent nitrogen atoms separated by more than two methylene groups must be brought close together, which contributes to the complexation reaction with endothermic energy [4]. The presence of propylene chains favours the formation of polynuclear assemblies (see diamines). The stability of complex **TRA1** is so high that the formation of $\mathrm{AgL_2}$ is prevented; steric strain is responsible for the absence of 1:2 species [4] in the Ag(I)-**TRA2** system.

The pentaamine **PA1** can form polynuclear complexes with Ag(I) in DMSO, although only ethylene chains separate the N atoms, due to the number of potential coordinating nitrogen atoms higher than the usual maximum coordination number (4) for Ag(I) in solution. The availability of one free aminoethylene branch in the $[\mathrm{AgL}]^+$ complex favours the formation of polynuclear species, in spite of the high stability of the 1:1 complex [20].

In water, N-alkylation of amine ligands shifts the redox potentials of the couples $\mathrm{M}^{n+1/n}\mathrm{L}_m$ anodically with respect to those of the corresponding non-alkylated complexes, stabilising Cu(I). For **TA1**, **TA6**, **TRA1** and **PA1**, an upper limit of stability constant values was given [41], based on the fact that no comproportionation was observed ($\log K_{1\,\mathbf{TA1}} < 10$, $\log K_{1\,\mathbf{TA6}} < 8$, $\log K_{1\,\mathbf{TRA1}} < 12$, $\log K_{1\,\mathbf{PA1}} < 13.4$), whereas $\log K_1$ values of 11.0 and 10.9 were found for **TRA2** and **PA2**. From these data, the authors [41] concluded that stabilisation of Cu(I) complexes by tertiary linear polyamines requires at least four tertiary N atoms. An increase in the number of donor nitrogen atoms to five (or even six) does not change this stabilisation to any significant extent. No data are available for Cu(I) in other solvents.

The data for Ag(I)-amine complex formation in DMSO, plotted in Fig. 4 as $\log \beta_{11}$ versus ΔH°_{11}, show a linear relationship

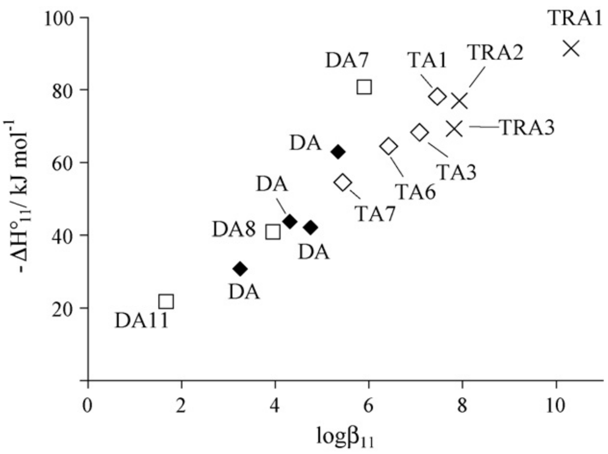

Fig. 4. $\log \beta_{11}$ vs. ΔH°_{11} (kJ mol^{-1}) for Ag(I)-polyamine complexation in DMSO: (◆) diamines forming five-membered rings; (□) diamines forming six-membered rings; (◇) triamines; (×) tetraamines. Values taken from Refs. [4,7,28,29].

between the stability of the complexes and the exothermicity of the reaction. This trend is more marked for the amines containing only ethylene chains between the nitrogen atoms. In particular; (i) both $\log \beta_{11}$ and ΔH°_{11} become more favourable as the number of N-donors in the ligand increases; (ii) ΔH°_{11} values show the same trend as $\log \beta_{11}$, i.e., they are less favourable when N-methylation increases in the same family of amines.

5. Formation of complexes with pyridine-based ligands

5.1. Coordination in water

Pyridine-containing ligands are characterised by a nitrogen donor, which is less basic than that of alkyl amines. The pK_a values of ethylamine and triethylamine in aqueous solution are 10.662 [125], and 10.68 [96] but that of pyridine (**P1**) is only 5.423 [162]. Regarding coordinating properties, pyridine behaves as a σ-donor with group 11 monovalent metal ions [65], although it is weaker than amines. In addition, when a pyridine moiety substitutes an aliphatic amine in a ligand, the whole structure acquires extra rigidity and less propensity to hydrogen bonding. All these features strongly decrease the solvation and stability of complexes with metal ions, generally producing a drop in $\log \beta$ values.

A consistent amount of stability data is available for the Ag(I)-**P1** system in water, whereas only a single paper is available for Cu(I) [2] and no literature data could be found for Au(I). **P1** forms only 1:1 and 1:2 complexes with Ag(I). The stability constants of **P1** of Ag(I) (Table 2; $\log \beta_{11} = 2.00$ and $\log \beta_{12} = 4.11$) are taken from [163], where enthalpy values are also present. In aqueous solution, Ag(I) complexes of pyridine are considered to be linear, as found for monoamines, although in pure pyridine EXAFS experiments demonstrate that Ag(I) is tetracoordinated [164]. In the solid state, both linear [165] and tetrahedral [64] Ag(I)-**P1** complexes are reported.

The Cu(I)-**P1** system has completely different speciation. In aqueous solution Cu(I) with **P1** can form up to four consecutive mononuclear complexes with $\log \beta_{1j}$ 3.9, 6.6, 7.9 and 8.77, respectively [152]. The higher affinity of **P1** for Cu(I) than for Ag(I) is expected, considering the ionic transfer functions water → PY of Ag(I) and Cu(I) ($\Delta G^\circ_{\mathrm{tr}}$ values of −57.1 and −11.5 kJ mol^{-1}, respectively) extracted from data in Table 1. Theoretical results for the formation of the 1:1 species in the gas phase qualitatively fit with this preference and predict the affinity order Ag(I) < Cu(I) < Au(I) [65].

Bipyridine **BP1**, due to its ability to form five-membered chelate complexes, forms more stable complexes than **P1** with both Ag(I) [166] and Cu(I) [152] (only $\log \beta_{12} = 13.18$ was measured in this case).

In water, amino-pyridine ligand **AP1** with Cu(I) forms two consecutive complexes with $\log \beta_{11} = 5.28$ and $\log \beta_{12} = 8.00$ [167]; a $\log \beta_{12}$ value = 10.66 was found for the formation of Cu(I)-**AP2** bis-complex in a 50% water/dioxan mixture [168].

The $\log \beta$ values for **AP1**-Ag(I) complexation are significantly lower than those of **BP1**-Ag(I) (Table 2), indicating that **AP1** coordinates Ag(I) only *via* its amine group, due to the high strain associated with the four-membered ring in the potential formation of the chelate complex. Thermodynamic data on Ag(I)-**AP2** complexation demonstrate that the lengthening by one unit of the chain connecting amino group to pyridine favours chelation, giving a complex which has an higher stability than that of **BP1** (according to the donor properties of the mixed ligand and its less important structural rigidity).

Coordination of **TP1** is again in line with the formation of a tri-chelate complex in [Ag**TP1**]$^+$, whereas $\log \beta_{12}$ for the bis-complex [Ag(**TP1**)$_2$]$^+$ is compatible with the formation of a five-coordinated complex similar to that observed in the solid state [169].

5.2. Coordination in aprotic solvents

Stability constants for complexes of Cu(I) with **P1** in AN ($\log \beta_{11} = 1.85$, $\log \beta_{12} = 2.52$, $\log \beta_{13} = 3.26$, at 293 K and $I = 0.1$ mol dm^{-3}) [170] are very low with respect to those found in water, reflecting the stronger solvation of Cu(I) in AN. The literature reveals that no further data exist for complexation reactions of Cu(I) by pyridine ligands in the other most common organic solvents.

In contrast, some papers focus on complexation of Ag(I) by pyridine and amino-pyridine ligands in DMSO [10,13,27]. In this solvent, as in water, **P1** with Ag(I) forms less stable and less exothermic complexes than monoamines [27]: this reflects the lower σ-donor ability of pyridine nitrogen compared with that of amines. As observed for amine ligand coordination in DMSO, pyridine ligand complexation is also enthalpy-driven (negative ΔH°_{ij}) with unfavourable entropic terms (Table 5).

Pyridine complexes are characterised by higher stability in water than in DMSO, the opposite of that found for primary and secondary aliphatic amines, in which the greater solvation of ligands in water overcomes the solvation of metal ions in DMSO (Table 1). In this case, the role of ligand solvation is evidently of minor importance, and stability constants follow the trend expected on the basis of metal ion solvation. The overall formation constants of the complexes formed by the Ag(I) ion with **P1**, **BP1** and **TP1** in DMSO, AN and PC, reported by Grzejdziak et al. [13], fit this conclusion: for **P1**, $\log \beta_{12\,\mathrm{PC}} = 5.01$, $\log \beta_{12\,\mathrm{water}} = 4.26$, $\log \beta_{12\,\mathrm{AN}} = 3.42$ and $\log \beta_{12\,\mathrm{DMSO}} = 1.96$, and follow the solvation order PC < water < AN < DMSO. For **BP1** and **TP1**, the order is the same, except for an inversion between water and PC for the latter ligand.

Destabilisation of the complexes on passing from water to DMSO is less marked in the case of amino-pyridines **AP2** and **BPA2**. This result confirms that the stability trend of the complexation reactions in the two solvents of this class of ligands depends on the desolvation/solvation of both metal ion and ligands, whereas metal solvation is more important for pyridine ligands.

Thermodynamic data for the first complexation step of **BP1** and **TP1** in DMSO, compared with those of **P1**, fit the formation of bi- and tri-chelated species. The ΔH°_{11} values for these reactions are lower than those expected for *n*-monodentate pyridines, because bi- and tridentate ligands are much more rigid and unable to arrange themselves for optimal binding of their N atoms [10].

When thermodynamic parameters for the first complexation steps of mono- and polypyridine ligands are compared with those of linear mono- and polyamines with the same number of donor atoms, $\Delta\log \beta_{11}$ ($\Delta\log \beta_{11} = \log \beta_{11\,\mathrm{amine}} - \log \beta_{11\,\mathrm{pyridine}}$) and $\Delta\Delta H^\circ_1$ ($\Delta\Delta H^\circ_{11} = \Delta H^\circ_{11\,\mathrm{amine}} - \Delta H^\circ_{11\,\mathrm{pyridine}}$) clearly increase more markedly with increasing ligand complexity (i.e., with the number of N-donors): $\Delta\log \beta_{11}$ and $\Delta\Delta H^\circ_{11}$ are 2.58, 3.26 and 6.47 log units, and −17.5, −42.8 and $-51.5\,\mathrm{kJ\,mol^{-1}}$ for the couples **A5** versus **P1**, **DA1** versus **BP1**, and **TA1** versus **TP1**, respectively (Tables 3–5). This effect is ascribed to the rigidity of the pyridine ligands, which have only limited possibilities of optimal arrangements around the metal centre and require higher energy for re-orientation of their donor groups.

The reaction entropy for pyridine ligands is systematically less unfavourable than for polyamines of the same denticity (e.g., **DA1** and **TA1**; Tables 3 and 4). This result is only partly due to the lower conformational freedom of polypyridines. An important factor which may explain such negative entropy for polyamines is the increase in local order around the complex, through the formation of new hydrogen bonds with surrounding solvent molecules. The results of pyridine and polypyridine studies [10] are indirect proof of this effect, since hydrogen bonding for complexed pyridines is not possible and the negative entropic contribution associated with it is missing.

Amino-pyridyl ligands display intermediate behaviour between that of polyamines and polypyridines [10]. Consequently, the thermodynamic parameters of Table 5 originate from a balance between the electronic and solvation effects of the two functions. From a structural point of view, they are closer to polyamines, due to their relatively high flexibility. **BPA2** forms dinuclear complexes in DMSO, like those found by single-crystal X-ray diffraction [10].

6. Conclusions

A large number of thermodynamic data on complexation of group 11 monovalent metal ions by open-chain N-donor ligands (amines, pyridines, amino-pyridines) has been reviewed. Due to the great instability of the 1+ oxidation state of Au in many solvents, the largest part of data presented in this review concerns Ag(I) complexation and, in limited extent, Cu(I).

Most of the complete thermodynamic data for Ag(I) complex formation are available in water and in DMSO and for this reason a great part of the discussions concerns these media and in minor extent, acetonitrile.

The stability constants and enthalpy of reactions are the result of a balance between solvation of the reacting species, donor properties of the ligands and steric factors. The solvation of the metal ion and the ligands is in competition with the formation of the complex: this will lead to expect a decrease in stability when the former is stronger. Often the effects on ligands and metal ion are balancing, as observed by comparing the data for Ag(I) in water and DMSO: primary and secondary polyamines form more stable complexes in DMSO because of the compensation between the solvation of metal (stronger in DMSO than in water) and ligand (weaker in DMSO). When the data for tertiary amines or pyridines, unable to form hydrogen bonds, are considered the effect of the metal solvation is largely dominant and the trends in stability go as expected on the basis of the strength of the metal solvation.

The alkyl substitution of the amines increases the inductive effect on the σ-donation, at the same time lowers the ability to form hydrogen bonds, stabilising the complex formed, and increases the steric strain of the structure. The sum of these factors leads to a general decrease in the stability of the complexes in the solvent media here discussed, as far as the number and size of the N-substituents increases. For polydentate ligands, also the increase of the ring size (from 5 to 6 membered) leads to a destabilisation of the chelate.

Pyridinic ligands show a behaviour similar to tertiary amines, even if their structure is more rigid, while amino-pyridines clearly display intermediate features between primary polyamines and pyridines.

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