ORIGINAL ARTICLE

Proton NMR study of the stoichiometry, stability and thermodynamics of complexation of Ag$^+$ ion with octathia-24-crown-8 in binary dimethylsulfoxide–nitrobenzene mixtures

Mojtaba Shamsipur · Mohsen Irandoust · Kamal Alizadeh · Vito Lippolis

Abstract Proton NMR was used to study the complexation reaction of Ag$^+$ with octathia-24-crown-8 (OT24C8) in a number of binary dimethylsulfoxide (DMSO)–nitrobenzene (NB) mixtures at different temperatures. In all cases, the exchange between free and complexed OT24C8 was fast on the NMR time scale and only a single population average ^{1}H signal was observed. The formation constants of the resulting 1:1 complexes in different solvent mixtures were determined by computer fitting of the chemical shift-mole ratio data. There is an inverse relationship between the complex stability and the amount of DMSO in the solvent mixtures. The enthalpy and entropy values for the complexation reaction were evaluated from the temperature dependence of formation constants. In all solvent mixtures studied, the resulting complex is enthalpy stabilized but entropy destabilized. The $T\Delta S°$ versus $\Delta H°$ plot of all thermodynamic data obtained shows a fairly good linear correlation indicating the existence of enthalpy–entropy compensation in the complexation reaction.

Keywords Octathia-24-crown-8 · Ag$^+$ · Proton NMR · Mixed solvent · Stoichiometry · Formation constant · Enthalpy · Entropy

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Introduction

According to the "hard–soft" acid–base theory, the complexing ability of crown ethers toward soft heavy metal ions is quite low [1–3]. However, the substitution of some oxygen atoms of crown ethers by sulfur atoms, results in a considerable increase in the stability of metal complexes with cations such as Ag$^+$, Hg^{2+} and Tl$^+$ ions in solution. Thus, the coordination chemistry of macrocyclic thioether ligands has received an increasing attention during the past two decades [4–8].

These ligands typically bind metal ions much more strongly than simple mono- or bidentate thioethers and, consequently, their use as ligating agents has permitted the synthesis of the first homoleptic thioether complexes of a wide variety of d- and p-block elements including Au$^+$, Ag$^+$, Cu^{2+}, Pb^{2+}, Cd^{2+} and Hg^{2+} ions [4–17]. Furthermore, because of their selective complex formation with soft transition and heavy metal ions as well as their negligible water solubilities, thiocrown ethers have been extensively used as suitable ion-carriers in solvent–solvent and solid phase extractions [17–21], ion-transport [22–25] and PVC-membrane ion-selective electrode studies [17, 26–29]. It is interesting to note that moderate π-acidity of thioethers [30] will result in the stabilization of lower oxidation states of transition and heavy metal ions to afford interesting complexes of unusual reactivity [4, 5, 7].

In the last decade, we have frequently used proton NMR as a powerful technique to study the thermodynamics and kinetics of complexation of several crown ethers, including some aza- and thiacrowns, in several non aqueous solvents and solvent mixtures [31–39]. In this work, we studied the stoichiometry and thermodynamics of complexation of Ag$^+$ with octathia-24-crown-8 (OT24C8) in a number of binary dimethylsulfoxide (DMSO)–nitrobenzene (NB) binary

mixtures, using the ^{1}H NMR technique. It should be noted that the crystalline structure of the polymeric 2:1 (metal-to-ligand) complex $\{[Ag_2(OT24C8)]^{2+}\}_\infty$ has already been reported in the literature [14]. However, to the best of our knowledge, there is no previous report available on the complexation of silver ion with OT24C8 in solution.
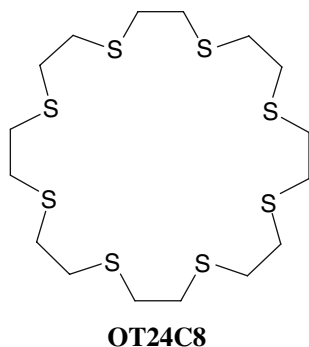
OT24C8

Experimental

Reagent grade OT24C8 (Aldrich) and silver nitrate (Fluka) were of the highest purity available and used without further purification except for vacuum drying. Reagent grade deuterated dimethylsulfoxide (DMSO, Merck) and extra pure nitrobenzene (NB, Merck) were used to prepare the solvent mixtures by weight.

^{1}H NMR spectra were recorded on a Bruker Avance (DPX) 200FT Spectrometer with a field strength of 4.7 Tesla (a frequency of 200.13 MHz) equipped with a temperature controller. In all experiments, TMS was used as an internal standard. The temperature of the probe was adjusted to an accuracy of ±0.1 °C using a heating element. Throughout the whole temperature range used, it was found that 10-min thermostatting prior to data collection was adequate for each sample to reach the equilibrium temperature.

Results and discussion

A series of binary DMSO–NM mixtures containing OT24C8 $(4.0 \times 10^{-3}\,\text{M})$ in the presence of different amounts of Ag^{+} were prepared and allowed to reach equilibrium, and then ^{1}H NMR spectra of the resulting solutions were recorded at 20.0, 30.0, 40.0 and 50.0 (±0.1) °C. At all mole ratios studied, only one population average ^{1}H signal was observed for HT24C8, indicating a fast exchange of the thiocrown ether between the free and the silver ion-complexed situation. Sample ^{1}H NMR spectra at various [Ag^{+}]/[OT24C8] mole ratios in 60% DMSO–40%

NB at 20.0 °C, showing a unique signal due to the –CH$_2$–CH$_2$ groups of the ligand, are shown in Fig. 1. The resulting chemical shift-mole ratio plots in pure DMSO and three different solvent mixtures of 80% DMSO–20% NB, 70% DMSO–30% NB, and 60% DMSO–40% NB at various temperatures are shown in Fig. 2.

An increase in the silver ion concentration gradually shifts the corresponding proton resonance of OT24C8 up-field, until a silver ion/OT24C8 mole ratio of about 1 is reached. This behavior is clearly indicative of the formation of a 1:1 complex in all solvent mixtures studied. Formation constants of the resulting 1:1 complexes were calculated by fitting, with the program KINFIT [40], the observed proton chemical shifts at various [Ag^{+}]/[OT24C8] mole ratios to a previously derived equation [41], which expresses the observed chemical shifts as a function of the complex formation constant, and the concentration of the free and complexed ligand. An example of computer fit is shown in Fig. 3 and all the K_f values calculated are summarized in Table 1. As it is seen from Fig. 3, there is a satisfactory agreement between the calculated and observed chemical shifts, supporting the formation of a 1:1 complex in solution.

To have a better understanding of the thermodynamic of the complexation reaction, it is useful to consider the
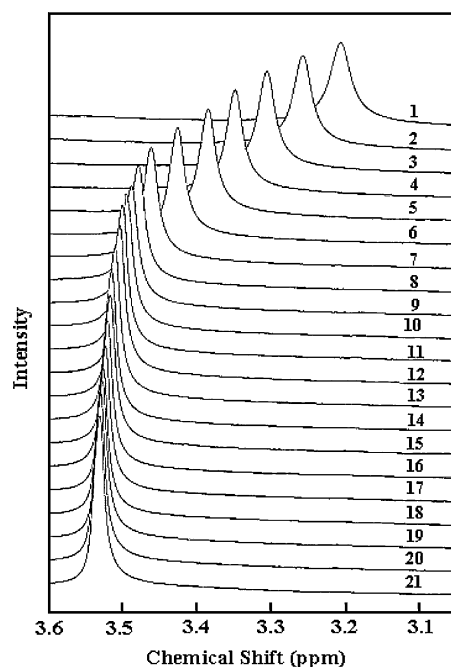

Fig. 1 Proton NMR spectra of OT24C8 at various [Ag^{+}]/[OT24C8] mole ratios in 40% NB–60% DMSO mixture at 20 °C. [Ag^{+}]/[OT24C8] mole ratios are: (1) 0.00, (2) 0.10, (3) 0.23, (4) 0.35, (5) 0.45, (6) 0.55, (7) 0.62, (8) 0.69, (9) 0.75, (10) 0.80, (11) 0.85, (12) 0.90, (13) 0.98, (14) 1.28, (15) 1.38, (16) 1.49, (17) 2.00, (18) 2.50, (19) 3.00, (20) 3.50, (21) 4.00

Fig. 2 Chemical shift mole ratio plots for complexation of Ag$^+$ with OT24C8 at different temperatures in (1) DMSO, (2) 80% DMSO, (3) 70% DMSO, and (4) 60%DMSO. Temperatures are: (**A**) 20 °C, (**B**) 30 °C, (**C**) 40 °C, (**D**) 50 °C
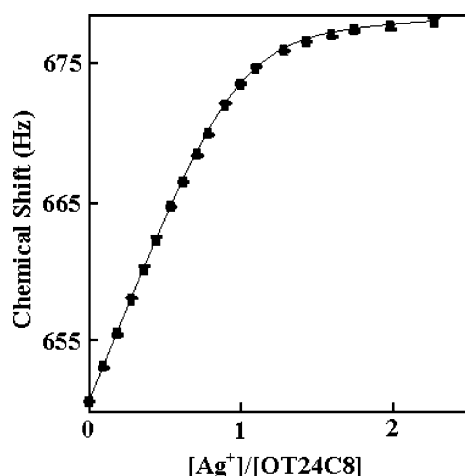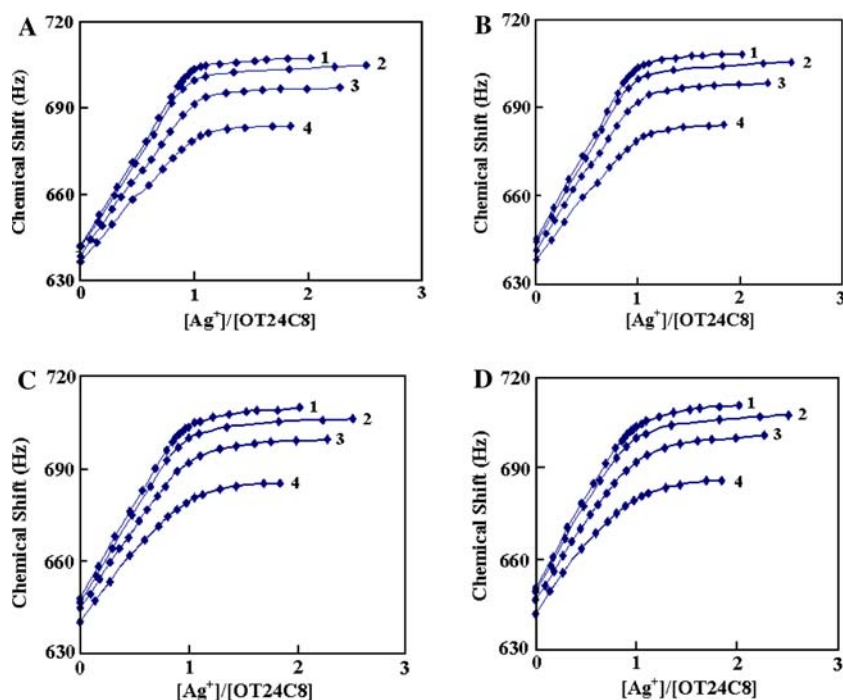
Fig. 3 Computer fit of the chemical shift mole ratio data for complexation Ag$^+$ with OT24C8 at 50 °C in 80% DMSO: (—) Experimental point, (■) theoretical point

enthalpic and entropic contributions of the reaction. The $\Delta H°$ and $\Delta S°$ values for the complexation reaction were evaluated from the temperature dependence of K_f by applying a linear least-squares analysis according the van't Hoff Eq. 1:

$$2.303 \log K_f = -(\Delta H°/RT) + (\Delta S°/R) \qquad (1)$$

The van't Hoff plots of log K_f versus $1/T$ for the complex in different solvent mixtures are shown in Fig. 4 and all $\Delta H°$ and $\Delta S°$ values, evaluated in the usual manner from the slope and intercept of the resulting linear plots, respectively, are also included in Table 1.

It is interesting to note that, Blake et al. have isolated in crystalline form a 2:1 metal-to-ligand complex between silver ion and OT24C8 from a CH$_2$Cl$_2$-acetonitrile mixture (1:1 v/v), using a 2:1 metal to ligand reaction molar ratio [14]. A single crystal X-ray structure determination [42] confirmed the product to be a one-dimensional polymer $\{[\text{Ag}_2(\text{OT24C8})]^{2+}\}_\infty$, in which each Ag$^+$ ion is coordinated to four S-donors in a distorted tetrahedral geometry. The four S-donors come from two different ligand molecules to generate an infinite ladder polymer along the b axis. Within the ladder, pairs of symmetry-related Ag$^+$ ions are coordinated between two macrocyclic ligands, so that all eight S-donors of each OT24C8 molecule are engaged in coordination. However, our solution studies, in solvent mixtures different from that used in the preparation of $\{[\text{Ag}_2(\text{OT24C8})]^{2+}\}_\infty$, revealed no evidence for the formation of a 2:1 complex in solution.

In order to obtain some information about the possible structures the 1:1 [Ag(OT24C8)]$^+$ complex, the molecular structures of the uncomplexed OT24C8 and that of its 1:1complex with Ag$^+$ ion were predicted by theoretical calculations, performed by employing the HYPERCHEM software version 7.0 [43]. The structure of the free ligand was calculated, starting from standard bond lengths and bond angles, and its geometry was fully optimized by minimizing the energy with respect to geometrical variables without any symmetry constraint, using the 3–21 G* basis set. The optimized structure of the ligand was then

Table 1 Formation constants and thermodynamic parameters for complexation Ag$^+$ with OT24C8 in binary DMSO–NB mixtures

Solvent	Log K_f (M^{-1})				$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})
	20 °C	30 °C	40 °C	50 °C			
100% DMSO	4.24 ± 0.06	4.06 ± 0.04	3.89 ± 0.05	3.76 ± 0.08	−28.8 ± 1.8	−23 ± 4	−21.7 ± 2.2
80% DMSO	4.49 ± 0.06	4.37 ± 0.04	4.17 ± 0.02	3.94 ± 0.02	−33.0 ± 2.8	−26 ± 5	−25.0 ± 3.2
70% DMSO	4.73 ± 0.11	4.51 ± 0.07	4.31 ± 0.04	4.12 ± 0.05	−36.3 ± 0.2	−33 ± 1	−26.0 ± 0.5
60% DMSO	4.99 ± 0.09	4.81 ± 0.07	4.52 ± 0.06	4.30 ± 0.07	−42.2 ± 1.9	−48 ± 4	−27.4 ± 2.4
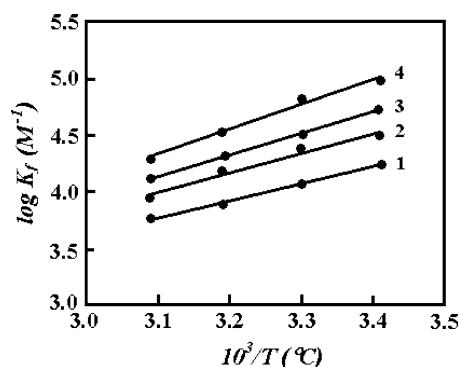
Fig. 4 van't Hoff plots for Ag$^+$–OT24C8 system in (1) DMSO, (2) 80% DMSO, (3) 70% DMSO, and (4) 60% DMSO

used to calculate the structure of its silver complex, using the ab initio calculations at the 3–21 G* level of theory without any symmetry restriction. The optimized structures of the ligand and its 1:1 silver ion complex are shown in Fig. 5.

The free ligand possesses an open more or less flat two-dimensional conformation in which SCH$_2$CH$_2$S moieties adopt linear arrangements with six S donors in exo and two in endo orientations. In the 1:1 complex with Ag$^+$ ion, the ligand is twisted around the silver ion with all donating sulfur atoms coordinated to the central metal ion, to form a three-dimensional 'wrap around' complex. The observation of a sharp singlet in the proton NMR spectra of the ligand

at all reaction molar ratios explored (see Fig. 1) would be consistent with this structure for the 1:1 complex formed in solution. A different structure for the 1:1 complex, in which some, but not all, of the sulfur atoms are coordinated to silver ion, is expected to result in a more complicated proton NMR spectrum.

The data given in Table 1 clearly illustrate the fundamental role of the solvent properties on the complexation reaction of Ag$^+$ ion with OT24C8. The stability of the complex increases with increasing the amount of nitrobenzene in the solvent mixture, at all temperatures studied. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number [44] plays an important role in complexation reactions [1, 2, 31–39]. DMSO is a solvent of high solvating ability (DN = 29.8), which can strongly compete with the thiacrown ether for Ag$^+$ ion. Thus, it can be expected that addition of NB as a low donicity solvent (DN = 4.4) to DMSO will increase the extent of interaction between the macrocycle's donor atoms and the silver ion. It should be noted that the somewhat lower dielectric constant of NB (34.8) in comparison with that of DMSO (45.0) would cause the electrostatic contribution to the bond formation to increase with increasing the amount of NB in the solvent mixture.

There is actually a linear relationship between log K_f of the complex [Ag(OT24C8)]$^+$ and the mole fraction of nitrobenzene (X_{NB}) in the mixed solvent, at all temperatures studied (Fig. 6). The same trend has already been

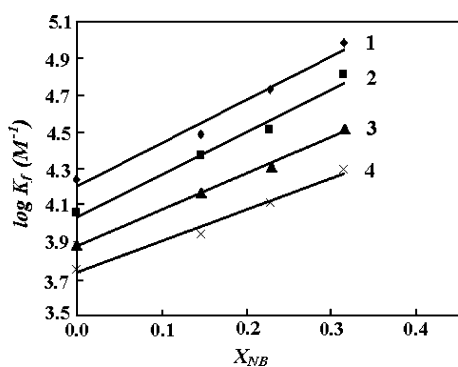**Fig. 5** Optimized structures of OT24C8 (**A**) and Ag$^+$-OT24C8 (**B**)
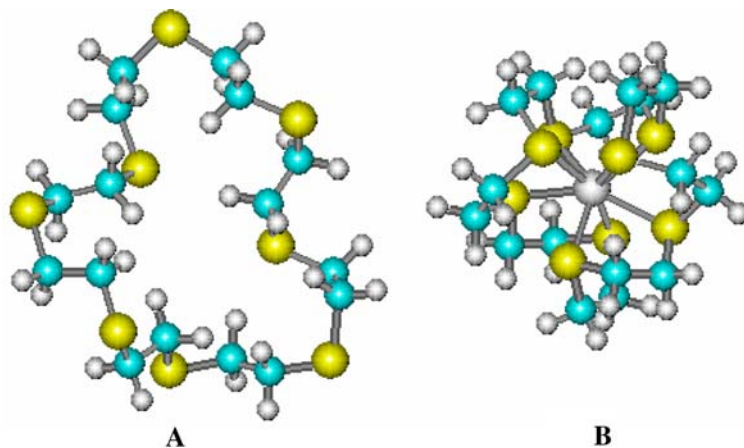
Fig. 6 Linear correlation between log K_f and mole fraction of NB (X_{NB}) in the complexation reaction of Ag^+ with OT24C8 at (1) 20 °C, (2) 30 °C, (3) 40 °C, and (4) 50 °C
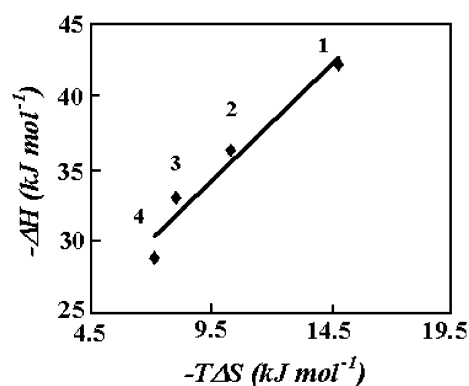

Fig. 7 Enthalpy–entropy compensation in complexation reaction of Ag^+ with OT24C8 in different DMSO-NB mixtures: (1) 60% DMSO, (2) 70% DMSO, (3) 80% DMSO, (4) 100% DMSO

reported for the formation of various complexes in different solvent mixtures [45–49]. It seems reasonable to assume that the preferential salvation of Ag^+ ion by DMSO is mainly responsible for such a monotonic dependence of the formation constants of the complex on the solvent composition.

The thermodynamic data in Table 1 revel that, in all solvent mixtures, the resulting $[Ag(OT24C8)]^+$ complex is enthalpy stabilized but entropy destabilized. It should be noted that, in the course of complexation reaction, the conformational change of the macrocyclic ligand from a rather flexible conformation in the free state to a rigid one in the complexed form (Fig. 5) results in the decreased entropy of the system [49, 50].

Table 1 shows that the thermodynamic data for the formation of the $[Ag(OT24C8)]^+$ complex vary significantly with the solvent properties. An increase in NB content of the solvent mixture results in the shift of both $\Delta H°$ and $\Delta S°$ values to more negative values. The competition of the solvent molecules with OT24C8 for Ag^+ ion is expected to decrease with increasing NB content of the solvent mixture: consequently, the cation-ligand interaction becomes stronger, resulting in more negative $\Delta H°$ values. On the other hand, as the cation-macrocycle binding becomes stronger, the degree of freedom of the resulting complex is diminished, mainly because of the increased rigidity of the complex structure. Thus, the negative change in entropy may cancel some of the enthalpic gain resulted from stronger binding.

A fairly good linear correlation between $\Delta H°$ and $T\Delta S°$ values, as it can be seen from Fig. 7, indicates the existence of an enthalpy–entropy compensation in the complexation reaction between Ag^+ ion and OT24C8 in the solvent systems studied. The existence of such a compensating effect between $\Delta H°$ and $\Delta S°$ values, which has been frequently reported for a variety of metal-ligand systems [48, 49, 51–53], would cause the overall change in Gibbs

energy of the complex to be smaller than might be expected from the change in either $\Delta H°$ or $\Delta S°$ independently.

References

1. Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., Christensen, J.J; Sen, D.: Thermodynamic and kinetic data for cation-macrocycle interaction. Chem. Rev. **85**, 271–339 (1985)
2. Izatt, R.M., Pawlak, K., Bradshaw, J.S., Bruening, R.L.: Thermodynamic and kinetic data for macrocycle interaction with cations and anions. Chem. Rev. **91**, 1721–2085 (1991)
3. Izatt, R.M., Pawlak, K., Bradshaw, J.S., Bruening, R.L.: Thermodynamic and kinetic data for macrocycle interaction with cations, anions, and neutral molecules. Chem. Rev. **95**, 2529–2586 (1995)
4. Cooper, S.R., Rawle, S.C.: Crown thioether chemistry. Struct. Bonding (Berlin) **72**, 1–72 (1990)
5. Glenny, M.W., van de Water, L.G.A., Vere, J.M., Blake, A.J., Wilson, C., Driessen, W.L., Reedijk, J., Schroder, M.: Improved synthetic methods to mixed-donor thiacrown ethers. Polyhedron **25**, 599–612 (2006)
6. Forsyth, G.A., Lockhart, J.C.: Criteria to judge preorganization study of known and the design of new thiocrown ethers. J. Chem. Soc. Dalton Trans. 2243–2249 (1994)
7. Danks, J.P., Champness, N.R., Schroder, M.: Chemistry of mixed nitrogen- and sulfur-donor and tridentate macrocycles. Coord. Chem. Rev. **174**, 417–468 (1998)
8. Madeu-Bulto, A.M., Dieguez, M., Artin, E.M., Gomez, M.: Chiral thioether ligands: coordination chemistry and asymmetric catalysis. Coord. Chem. Rev. **242**, 159 (2003)
9. Blake, A.J., Halcrow, M.A., Schroder, M.: Organometallic macrocyclic chemistry - Synthesis of cationic half-sandwich iridium(I) complexes of 1,4,7-trithiacyclononane ([9]aneS3) - Crystal-structures of [Ir([9]aneS3)(C_2H_4)]PF_6, [Ir([9]aneS3)(C_8H_{12})]PF_6 and [Ir([9]aneS3)(C_4H_6)]PF_6.0.5et2O. J. Chem Soc. Dalton Trans. 1631–1639 (1994)
10. Kim, H.-J., Lee, J.H., Suh, I.H., Do, Y.: A novel route to dinuclear heteroleptic rhodium(III) complexes of 1,4,7-trithiacyclononane. Inorg. Chem. **34**, 796–801 (1995)
11. Grant, G.J., Rogers, K.E., Setzer, W.N., Van Derveer, D.J.: Crown thioether complexes of trivalent transition-metal ions - The crystal-structure of [cr(18S6)Cl-3]. Inorg. Chim. Acta **234**, 35–45 (1995)

12. Landgrafe, C., Sheldrick, W.S.: Dinuclear thioether half-sandwich ruthenium(II) complexes of the types [{RuL'([9]aneS(3))}$_{(2)}$(mu-L)$_{(n)}$]$^{(2+)}$ (n=1, L' = PPh(3); n=2, L'=MeCN), [{Ru([9]aneS(3))}$_{(2)}$(mu-L)$_{(2)}$]$^{(2+)}$ and [{Ru([9]aneS(3))}$_{(2)}$ (mu-L)$_{(3)}$]$^{(+)}$ with heterocyclic thioamides L ([9]aneS(3)=1,4,7-trithiacyclononane). J. Chem. Soc. Dalton Trans. 989–998 (1996)

13. Adams, R.D., Fallen, S.B., Perrrin, J.L., Queisser, J.A., Yamamoto, J.H.: The catalytic ring-opening of cyclooligomerization (ROC) of thietane by the complexes M(CO)$_{(5)}$L (M=Cr and W; L=CO, thietane and 1,5,9-trithiacyclododecane). Chem. Ber. 129, 313–318 (1996)

14. Blake, A.J., Li W.-S., Lippolis, V., Taylor, A., Schroder, M.: Mercury(II), silver(I) and gold(I) thioether crown chemistry: Synthesis, electrochemistry and structures of [(HgBr$_2$)$_{(2)}$([24] aneS(8))], [{Ag$_2$([24]aneS(8))(CF$_3$SO$_3$)$_{(2)}$ (MeCN)$_{(2)}$}(infinity)], [Ag$_2$([28]aneS(8))][NO$_3$]$_{(2)}$ and [Au$_2$([28] aneS(8))] [PF$_6$]$_{(2)}$ ([24]aneS(8) = 1,4,7,10,13,16,19,22-octathia-cyclotetracosane; [28]aneS(8) = 1,4,8,11,15,18,22,25-octathiacyclo-octacosane). J. Chem. Soc. Dalton Trans. 2931–2937 (1998)

15. Blake, A.J., Lippolis, V., Parsons, S., Schroder, M.: Catena-poly[[trans-dichloro-copper(II)]-mu-1,4,7,10,13,16-hexathia-cyclooctadecane-S-1:S-10]. Acta Crystallogr. C 57, 36–37 (2001)

16. Naito, T., Nishibe K., Inabe T.: New binuclear copper complexes [(9S3)Cu(CN)Cu(9S3)]X$_n$ (X=BF$_4$, n=1; X=TCNQ, n=2) (9S3=1,4,7-trithiacyclononane): Syntheses, crystal structures and magentic properties: Z. Anorg. Allg. Chem. 630, 2725–2730 (2004)

17. Lippolis, V., Shamsipur, M.: Synthesis, coordination properties and analytical applications of mixed donor macrocycles containing the 1,10-phenanthroline sub-unit. J. Iran. Chem. Soc. 3, 105–127 (2006)

18. Saito, K., Murakami, S., Muromatsu A., Sekido E.: Extraction behavior of silver(I) with some cyclic tetrathioethers. Polyhedron 12, 1587–1591 (1993)

19. Moyer, B.A., Delmau, L.H., Case, G.N., Bajo, S., Baes, C.F.: Comprehensive equilibrium-analysis of the complexation of Cu(II) by tetrathia-14-crown-4 in a synergistic extraction system employing didodecylnaphthalene sulfonic-acid. Sep. Sci. Technol. 30, 1047–1069 (1995)

20. Yamini, Y., Alizadeh, N., Shamsipur, M.: Solid phase extraction and determination of ultra trace amounts of mercury(II) using octadecyl silica membrane disks modified by hexathia-18-crown-6-tetraone and cold vapor atomic absorption spectrometry. Anal. Chim. Acta. 355, 69–74 (1997)

21. Shamsipur, M., Mashhadizadeh, M.H.: Preconcentration of trace amounts of silver ion in aqueous samples on octadecyl silica membrane disks modified with hexathia-18-crown-6 and its determination by atomic absorption spectrometry. Fresenius J. Anal. Chem. 367, 246–249 (2000)

22. Shamsipur, M., Mashhadizadeh, M.H.: Highly efficient and selective membrane transport of silver(I) using hexathia-18-crown-6 as a specific ion carrier. Sep. Purif. Technol. 20, 147–153 (2000)

23. Shamsipur, M., Azimi, G., Mashhadizadeh, M.H., Madaeni, S.S.: Selective transport of silver ion through a supported liquid membrane using hexathia-18-crown-6 as carrier: Anal. Sci. 17, 491–495 (2001)

24. Mashhadizadeh, M.H., Mohyaddini, R., Shamsipur, M.: Selective and efficient liquid membrane transport of Au(III) by tetrathia-12-crown-4 as a specific carrier. Sep. Purif. Technol. 39, 161–166 (2004)

25. Shamsipur, M., Hashemi, O.R., Lippolis, V.: A supported liquid membrane system for simultaneous separation of silver(I) and mercury(II) from dilute feed solutions. J. Membr. Sci. 282, 322–327 (2006)

26. Fakhari, A.R., Ganjali, M.R., Shamsipur, M.: PVC-based hexathia-18-crown-6-tetraone sensor for mercury(II) ions. Anal. Chem. 69, 3693–3696 (1997)

27. Mashhadizadeh, M.H., Shamsipur, M.: Silver(I)-selective membrane electrode based on hexathia-18-crown-6. Anal. Chim. Acta. 381, 111–116 (1999)

28. Shamsipur, M., Mashhadizadeh, M.H.: Cadmium ion selective electrode based on tetrathia-12-crown-4. Talanta. 53, 1065–1071 (2001)

29. Mashhadizadeh, M.H., Mostafavi, A., Razavi, R., Shamsipur, M.: Highly selective and sensitive Cu(II) PVC membrane electrode based on 3,6,9,14-tetrathiabicyclo[9.2.1.]tetradeca-11,13-diene as a suitable neutral ionophore. Sens. Actuators B 86, 222–228 (2002)

30. Murray, S.G., Hartley, F.R.: Coordination chemistry of thioethers, selenoethers, and telluroethers in transition-metal complexes. Chem. Rev. 81, 365–414 (1981)

31. Alizadeh, N., Shamsipur, M.: Nuclear magnetic resonance study of the ligand interchange of 18-crown-6 complexes with La^{3+}, Ca^{2+}, Pb^{2+} and Ba^{2+} ions in 70% methanol solution. J. Chem. Soc. Faraday Trans. 92, 4391–4394 (1996)

32. Alizadeh, N., Shamsipur, M.: Nuclear magnetic resonance study of the ligand interchange of Ba^{2+}-18-crown-6 complex in methanol solution. J. Solution Chem. 25, 1029–1039 (1996)

33. Fakhari, A.R., Shamsipur, M.: An NMR study of the stoichiometry and stability of lithium ion complexes with 12-crown-4, 15-crown-5 and 18-crown-6 in binary acetonitrile-nitrobenzene mixtures. J. Incl. Phenom. 26, 243–251 (1996)

34. Shamsipur, M., Alizadeh, N.: NMR study of the ligand interchange of hexacyclen and hexamethylhexacyclen complexes with Tl$^+$ ion in 70% methanol solution. J. Chin. Chem. Soc. 45, 241–247 (1998)

35. Fakhari, A.R., Shamsipur, M.: Proton NMR study of the ligand interchange of the Ba^{2+}-18-crown-6 complex in binary acetonitrile-water mixtures. J. Incl. Phenom. 32, 405–414 (1998)

36. Shamsipur, M., Talebpour, Z., Alizadeh, N.: NMR study of the stoichiometry, stability and ligand interchange of silver ion-hexathia-18-crown-6 complex in binary dimethylsulfoxide-acetonitrile and dimethylsulfoxide-methanol solvent mixtures at 300 K. J. Solution Chem. 32, 227–238 (2003)

37. Talebpour, Z., Alizadeh, N., Bijanzadeh, H.R., Shamsipur, M.: Cadmium-113 NMR and theoretical studies of complexation of 15-crowns-5 and benzo-15-crown-5 in acetonitrile and its binary mixtures with water and nitromethane. J. Incl. Phenom. 49, 101–106 (2004)

38. Alizadeh, N., Bordbar, M., Shamsipur, M.: Proton NMR investigation of the stoichiometry, stability and exchange kinetics of Tl$^+$ complexes with hexacyclen and hexamethylhexacyclen in dimethylformamide solutions. Observation of a three site exchange process. Bull. Chem Soc. Jpn. 78, 1763–1772 (2005)

39. Bordbar, M., Shamsipur, M., Alizadeh, N.: ^{1}H NMR studies of homo and mixed ligand complexes of Tl$^+$ ion with several polyazamacrocycles. Bioorg. Med. Chem. 13, 2253–2262(2005)

40. Nicely, V.A., Dye, J.L.: A general purpose curve fitting program for class and research use. J. Chem. Educ. 48, 443–447 (1971)

41. Cahen, Y.M., Dye, J.L., Popov, A.I.: Lithium-7 nuclear magnetic resonance study of lithium cryptates in various solvents. J. Phys. Chem. 79, 1289–1291 (1975)

42. Blake, A.J., Li W.-S., Lippolis, V., Schroder, M.: Thioether macrocycles as spacers for crystal engineering: synthesis and crystal structures of [Ag$_2$([24]aneS(8))(CF$_3$SO$_3$)$_{(2)}$(MeCN)$_{(2)}$] (infinity) and [Ag([16]aneS(4))(BF$_4$)] (infinity)([24]aneS(8) = 1,4,7,10,13,16,19,22-octathiacyclotetracosane; [16]aneS(4) = ,1, 5,9,13-tetrathiacyclohexadecane). Chem. Commun. 1943–1944 (1977)

43. Hyperchem, Release 502, Hypercube, Inc., Gainesville, 1997
44. Gutmann, V.: Coordination Chemistry in Nonaqueous Solvents, Springer-Verlag, Vienna, 1968
45. Izatt, R.M., Terry, R.E., Nelson, D.P., Chan, Y., Eatough, D.J., Bradshaw, J.S., Hansen, L.D., Christensen, J.J.: Calorimetric titration study of the interaction of some uni- and bivalent cations with benzo-15-crown-5, 18-crown-6, dibenzo-24-crown-8, and dibenzo-27-crown-9 in methanol-water solvents, at 25.degree C and mu = 0.1. J. Am. Chem. Soc. **98**, 7626–7630 (1976)
46. Cox, B.G., Firman, P., Gudin, D., Schneider, H.: Potentiometric and proton NMR studies on the solvation of cryptand (222) and its complexes with potassium(1+) and silver(1+) in acetonitrile water mixtures. J. Phys. Chem. **86**, 4988–4992 (1982)
47. Rouhollahi, A., Amini, M.K., Shamsipur, M.: NMR study of the stoichiometry, stability and exchange kinetics of complexation reaction between Pb^{2+} ion and18-crown-6 in binary acetonitrile-water mixtures. J. Solution Chem. **23**, 63–74 (1994)
48. Ghasemi, J., Shamsipur, M.: Conductance study of some transition and heavy metal complexes with 1,10-diaza-18-crown-6 in binary acetonitrile-dimethylsulfoxide mixtures. J. Solution Chem. **25**, 485–504 (1996)
49. Shamsipur, M., Pouretedal, H.R.: Conductance study of complexation of lead ions with several 18-membered crown ethers in binary acetonitrile-dimethylsulfoxide mixtures between 25 and 55 °C. J. Solution Chem. **28**, 1187–1205 (1999)
50. Shamsipur, M., Popov, A.I.: Multinuclear NMR study of dibenzo-30-crown-10 complexes with sodium, potassium, and cesium ions in nonaqueous solvents. J. Am. Chem. Soc. **101**, 4051–4055 (1979)
51. Inoue, Y., Takushi, T., Liu, Y., Tong, L.-H., Lin, D.S.: Thermodynamics of molecular recognition by cyclodextrins. 1. Calorimetric titration of inclusion complexation of naphthalene-sulfonates with alpha-cyclodextrin, beta-cyclodextrin, and gamma-cyclodextrin - Enthalpy entropy compensation. J. Am. Chem. Soc. **115**, 475–481 (1993)
52. Visser, H.C., Reinhoudt, D.N., de Jong, F.: Carrier-mediated transport through liquid membranes. Chem. Soc. Rev. 75–82 (1994)
53. Grunwald, E., Steel, C.: Solvent reorganization and thermodynamic enthalpy-entropy compensation. J. Am. Chem. Soc. **117**, 5687–5692 (1995)