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Complexation of Cyclic and Acyclic Polyethers with Lanthanides and Picrate As Counter Anion

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Abstract

Lanthanides (Ln) are very interesting class of metal due to their flexibility in the formation of coordination compounds. Lanthanide-picrate complexes with cyclic (18-crown-6) and acylic (pentaethylene glycol = EO5) ligands (L), having six oxygen donor atoms were prepared and characterized by elemental analysis, IR and NMR. In the present paper the crystal structure of four new cyclic and acyclic complexes of Nd and Eu, namely $[Nd.EO5.(pic)_2]^+[pic]^-$ **(a)**; $[Eu.EO5.(pic)_2]^+[pic]^-$ **(b)**; $[Nd.18C6.(pic)_2]^+[pic]^-$ **(c)**; $[Eu.18C6.(pic)_2]^+[pic]^-$ **(d)** are compared and contrasted. The observation between complex systems of Ln-18C6-pic and Ln-EO5-pic with the same number of oxygen atoms of ether linkages revealed some interesting phenomena. The most distinct difference observed was on the coordination numbers, the molecular structure of the acyclic **(a)** and **(b)** complexes exhibited nine coordination numbers by six oxygen atoms from EO5 and two from one bidentate and one monodentate picrates, while the cyclic **(c)** and **(d)** complexes show ten coordination numbers by six oxygen atoms from 18C6 and four from two bidentate picrates. The higher thermal stability of complexes **(c)** and **(d)** relative to **(a)** and **(b)** is due to the presence of the cyclic ligand and intermolecular C–H···O hydrogen bond in the former, but not in the latter.

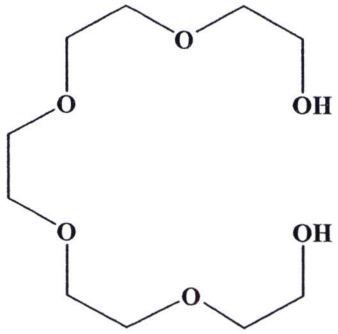
Key words: 18-Crown-6, Pentaethylene glycol, picrate complex, Neodymium, Europium, Coordination number, Hydrogen bonding.

Introduction

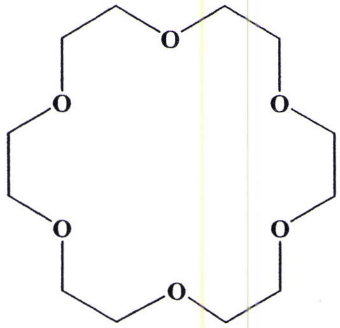
Crown ethers are characterized by a cyclic carbon structure, containing heteroatoms such as oxygen, nitrogen, sulphur, phosfor, which provide an electron-rich environment for solutes, some of which may fit into the central cavity of the molecule forming stable complexes [1,2]. Crown ethers and polyethylene glycols (PEG) have been reported to form many complexes with lanthanides and several counter anions. Roger *et al.* [3-5] have isolated and found crown ethers complexes with lanthanide chloride and nitrate. Hirashima *et al.* [6,7] have reported the structure of polyethylene glycol complexes with lanthanide nitrate and chloride, while, Yao *et al.* [8] reported polyethylene glycol complexes with lanthanide perchlorate as the counter anion. Crystal structure of these acyclic polyether complexes adopted cyclic "crown-like" conformation.

The flexibility of the coordination sphere of lanthanide ions, coupled with the tendency of lanthanides to adopt high coordination numbers, makes the lanthanide ions attractive for discovery of unusual topology [9]. Such thermodynamically and kinetically stable Ln(III) compounds generally require high density ligands with hard donors such as oxygen and nitrogen atoms [9] for complexation.

Recently we have reported the structure of lanthanide picrate-pentaethylene glycol of praseodymium [10]. We found that the EO5 ligand (Compound I) has a crown like (Compound II) character in wrapping the Ln(III) and has nine coordination numbers, which is a common coordination number for lanthanide ions. The coordination chemistry of lanthanides and crown ether ligands with bulky counter anion, i.e. picric acid (PicH) have not been reported. With the scarcity of the works reported on the structure of the complex formed in the availability of multiple donor atoms with lanthanides and the complexation behavior of cyclic and acyclic polyethers and lanthanide encourage us to pursue this study.



Compound I



Compound II

Experimental

Chemical and physical measurements

All reagents were commercially available and used without further purification: 18-crown-6, 99 % (Fluka), picric acid (Hpic), > 99.8 % (BDH) and Ln_2O_3 (Aldrich). Lanthanide-nitrate salts (Nd and Eu) were prepared from their corresponding oxides, Ln_2O_3 (Aldrich) by the action of nitric acid, 65 % (Aldrich).

Elemental analyses were performed on a Control Equipment Corporation elemental analyser Model 250-XA, USA. Infrared (IR) spectra were recorded in the 4000 – 400 cm^{-1} region using Perkin-Elmer 2000 FTIR spectrometer, by the KBr pellets method. ^1H NMR measurement was made on a Bruker 300 MHz NMR spectrometer in D_2O and acetone-*d* solvents. Melting points were determined using Gallenkamp melting point apparatus. The thermal stability of the complexes was measured under nitrogen atmosphere at scan rate of 30 °C/min using a Perkin-Elmer TGA-7.

General preparations of lanthanide EO5 complexes

To a solution of EO5 (0.60 g, 2.52 x 10^{-3} mol) in 10 mL of acetonitrile-methanol (3:1 v/v), picric acid (0.91 g, 3.97 x 10^{-3} mol) in 5 mL of acetonitrile-methanol (3:1 v/v) was added drop wise with stirring until a yellow clear solution was obtained. To this solution an appropriate hydrated lanthanide nitrate solution (1 x 10^{-3} mol) in 10 mL acetonitrile-methanol (3:1 v/v) was added drop-wise at room temperature (30 °C). The resulting mixture (Nd or Eu) were then filtered and transferred to small flask (50 mL) covered with aluminum foil to which small holes were made to control the solvent evaporation. Single crystals suitable for X-ray investigation were obtained by slow evaporation after five days. The yields obtained for Nd 0.527 g (27 %) and Eu 0.039 g (2 %). Elemental analysis for Nd **(a)**: Found. (Calc.) C, 31.66 (31.36); H, 2.41 (2.52) and N, 11.52 (11.76) %; m.p. 263°C, color: deep yellow. For Eu **(b)**: C, 31.26(31.19); H, 2.56(2.69) and N, 11.42(11.69) %; m.p. 257.1°C, color: yellow.

General preparations of lanthanide 18C6 complexes

Nd and Eu-picrates were prepared following the procedure described by Harrowfield *et al.* [11]. Lanthanide-picrate 0.221 g (0.21 x 10^{-3} mol) and 18-crown-6 0.264 g (1 x 10^{-3} mol) were dissolved in 20 mL hot acetonitrile while heating on the steam bath for 15 min. The flask was then cooled at room temperature to allow slow evaporation of the solvent. Single crystals grew in the solution after one day. The yields obtained for Nd 0.06 g (12 %) and Eu 0.025 g (5 %). Elemental analysis for Nd **(c)**: Found. (Calc.) C, 32.61 (32.85); H, 2.80 (2.74) and N, 11.21 (11.49) %; m.p. 289°C, color: deep yellow. For Eu **(d)**: C, 32.27 (32.62); H, 2.57 (2.72) and N, 11.23 (11.43) %; m.p. 278.2°C, color: orange.

X-ray crystallography

The determination of the molecular structure of the complexes were performed on a 1K-SMART CCD diffractometer using graphite-monochromator Mo Kα radiation ($\lambda = 0.71069$ Å) with a detector distance of 5 cm and swing angle of minus 35° at 293 K. A summary of the crystallographic data for the [Ln.(pic)$_3$L] complexes are summarized in Table 1. The selected bond lengths and bond angles of the [Ln.(pic)$_3$L] complexes are listed in Table 2 and Table 3. The structure was solved by direct methods and refined by least square on Fo^2 using the SHELXTL software package [12, 13].

Results and Discussions

From the elemental analysis, the stoichiometry of the acyclic and cyclic complexes were confirmed to be 1:3:1 (ligand/picrate/Ln). The complexes are very soluble in MeCN, less soluble in MeOH, and insoluble in CHCl$_3$. It is ionic with the molecular formula of $[Ln.(L).(pic)_2]^+[pic]^-$, where L = EO5 or 18-crown-6.

IR spectrum

The IR spectra of the complexes, the free ligand and picrate counter anion are shown Figure 1. The infrared spectra of the free acyclic ligand showed very strong band at 2874 cm^{-1} due to C-H stretching while for the free cyclic ligand at 2889 cm^{-1}. In the spectra of acyclic complexes the band at 2874 cm^{-1} is reduced into a weak band due to its transformation to cyclic conformation. The vibration mode of the ethylene ether (C–O–C) is shifted to lower frequencies from 1635s to 1615s cm^{-1} in 18C6 complexes and 1650s to 1610s cm^{-1} in EO5 complexes, respectively, indicating the coordination is through the carbonyl oxygen (C–O). The larger band shifts for ν(C–O) of 40 cm^{-1} in the acyclic complexes suggested that the $Ln–O_{phenolic}$ bonds are stronger than $Ln–O_{ligand}$ bonds. For the cyclic complexes a shift of 20 cm^{-1} suggested that the $Ln–O_{phenolic}$ bonds are stronger than $Ln–O_{ligand}$. In addition, the observed vibration of ν(C–O) at 1296 cm^{-1} for acyclic and 1270 cm^{-1} for cyclic complexes of **(a)**, **(b)**, **(c)** and **(d)**, respectively, indicating that all the ether oxygen atoms are involved in the coordination to Ln(III) ion. The H atom of the OH groups in free picric acid was replaced by Ln(III) as 1155 cm^{-1} bending vibration of the OH disappeared in the spectra of the complexes. The presence of $\nu_{as}(NO_2)$ (1578s and 1534s cm^{-1}) and $\nu_s(NO_2)$ (1370s and 1338s cm^{-1}), indicates the different in coordination modes involving the phenolic and *ortho*-nitro group oxygen atoms, as observed by Yongchi *et al.* [14].

NMR spectrum

^{1}H NMR spectra of the polyether and its complexes are not similar. The spectrum of 18C6 exhibits only one peak at 3.656s ppm due to its symmetric compound. However, the spectrum of the EO5 ligand exhibits three peaks at 3.70s, 3.45t and 3.41s ppm. The bands at 3.41 and 3.45 ppm represent the methylene (CH_2) protons, whereas the band at 3.70 ppm exhibited the terminal OH groups. The (CH_2) protons at 3.41 ppm on the free ligand were shifted to the downfield by $\Delta\delta$: – 0.14 and – 0.197 ppm for Nd **(a)** and Eu **(b)**, respectively upon complexation. However, for the cyclic complexes spectra band at 3.656 ppm were shifted to the upfield by $\Delta\delta$: 0.809 and 0.788 ppm, respectively for Nd **(c)** and Eu **(d)** complexes.

A singlet peak is also observed at 8.90s and 8.84s ppm for Nd **(a)** and Eu **(b)** complexes, respectively, representing the protons of benzene on the picrate, indicating the fast exchange among the group in solution [15]. This peak was shifted identically (0.22 - 0.28) ppm for all the complexes relating to the protons of the benzene (9.12 ppm) on the free picric acid. Therefore, in the cyclic complexes the signal was shifted to higher field at 11.92s and 10.35t ppm upon coordination, respectively, for Nd **(c)** and Eu **(d)** complexes. The chemical shift was observed to be higher for the cyclic complexes **(c)** and **(d)** than the acyclic complexes **(a)** and **(b)**. The difference was due to the different in coordination, in which very dependent on the second picrate counter anion, whereby the acyclic complexes are monodentate while the cyclic complexes are bidentate.

Thermal stability

The complexation and decomposition of the acyclic polyethers and its complexes with metal ions are generally faster than cyclic polyethers [16]. The decomposition of the free acyclic ligand begins at 165°C and take place in only a single step. The strong endothermic peak at 340°C on the DTG curve shows maximum loss of weight of the free EO5 ligand upon heating. However, the cyclic ligand also exhibited single step weight-loss starting at 105°C and the strong endothermic peak at 235°C. The thermograms for both **(a)** and **(b)** complexes are similar (three steps weight-loss). However, the cyclic complexes showed different steps, namely three for **(c)** and four for **(d)**. The acyclic complexes rapidly lost most of their weight in the range of 220 to 300°C. On the other hand, the cyclic complexes need higher temperature to decompose and weight lost was steadily observed from 270 to 320°C (Figure 2).

The decomposition of the complexes was also found to be dependent on the radii of the metal ions. The residue of the neodymium complexes **(a)** and **(c)** remain about 7 and 4 %, respectively, whereas in the case of europium complexes namely **(b)** and **(d)** the residue are 10 and 5 %, respectively. The rate of decomposition of the Eu complexes was slower than Nd complexes. These findings indicated that the ligand remain intact with the lanthanide ions up to this range of temperature, followed by the decomposition of the complex as well as the ligand itself, and finally left with lanthanide oxides as residue. Very strong endothermic peaks appeared at 285, 290, 320 and 313°C for **(a)**, **(b)**, **(c)** and **(d)** complexes, respectively.

Crystal structure

In principle, the complexes contained three picrate anions, but only two picrate anions were found to be bonded ionically with Ln(III) through oxygen atoms from hydroxyl of the phenolic group. However, the third picrate anion is solvated. Thus, the acyclic and cyclic complexes having molecular formula of $\{[Ln.L.(pic)_2]^+[pic]^-\}$, where L = EO5 and 18C6.

The crystal systems between cyclic and acyclic complexes are not similar. In the cyclic complexes with orthorhombic crystal system in the *Pbca* structure with eight molecules in the unit cell whereas in the acyclic complexes with monoclinic crystal system in the $P2_1/c$ structure with four molecules in the unit cell. The **(a)** and **(b)** are nine coordination numbers complexes with six oxygen atoms from EO5, two from bidentate and one from monodentate picrates. Whereas, for **(c)** and **(d)** they are ten coordination numbers complexes with six oxygen atoms from cyclic ligand, four from two bidentate picrates. The coordination of each picrate occurs by the phenoxo oxygen and one oxygen of one of the *ortho* nitro group which occupy the capping positions on the square phases of the tricapped trigonal prismatic [17] for **(a)** and **(b)** complexes and bicapped square antiprismatic [17] for **(c)** and **(d)** complexes. This nature of interaction indicates that the lanthanide ions are more oxophilic than nitrophilic [10].

The linear acyclic polyether (EO5) is predicted to resemble the ring when the complex formed and we predict the radius is 2.29 Å (total bond length to make a circumference and thus the radius is calculated). The radius of the cyclic polyether (18C6) is slightly shorter, namely 1.30 Å. Nevertheless, bond lengths of Ln–O are almost similar in both complexes (Table 2). The lanthanide ion is not localized in the center of the cyclic ligand (Figure 3a), this manifested in the significant difference in the bond lengths of Ln–O (2.482 to 2.597 Å). Similarly, in the acyclic **(a)** and **(b)** complexes the metal ion is not located at the center of acyclic ligand, therefore a significant difference of the bond lengths of Ln–O for both complexes are also observed (2.459 to 2.546 Å) with the mean of **(a)** is 2.501 and **(b)** is 2.461 Å, respectively. The average distance between Ln–O for compounds **(c)** and **(d)** are 2.534 and 2.523 Å, respectively. It was observed that the cyclic complexes have longer Ln–O bonds than acyclic complexes.

The distance of Ln–$O_{phenolic}$ are shorter than of Ln-O_{ligand} namely 2.352 Å for **(a)** and 2.307 Å for **(b),** and 2.357 and 2.298 Å for **(c)** and **(d)** complexes respectively, this due to the higher electron density on the oxygen from phenolic picrate.

The mean of bond lengths Ln–O_{ligand} are 2.505, 2.545, 2.516 and 2.540 Å for **(b), (d), (a)** and **(c),** respectively, significantly shorter than the bond lengths of Ln–O_{nitro} of 2.546, 2.575, 2.675 and 2.769 Å for **(b), (a), (c)** and **(d)**, respectively. This suggested the Ln–O_{ligand} bond is stronger than Ln–O_{nitro} bond. From the observation in Table 3 in the acyclic complexes interaction between the terminal OH groups have bond angles are bigger than the cyclic complexes namely 71.63(10)°, 71.87(7)°, 64.44(7)°, 62.03(11)°, respectively, for **(a)**, **(b)**, **(c)** and **(d)** complexes.

The C–O bond length decreases from 1.327 Å for free acid to 1.273, 1.268, 1.271 and 1.267 Å for **(a)**, **(b)**, **(c)** and **(d)** complexes, respectively. This shortening suggested a tendency of picrate anion to show a quinone-like structure [18-24]. The N–O bond distance for the oxygen atoms coordinated to the Ln(III) is slightly influenced by the chelation because generally the N–O bond distance is 1.223 Å. However, the N–O bond distance increases to 1.236 Å for both the acyclic and the cyclic complexes.

Hydrogen bonding between the H and O atoms in intermolecular system of the polyether complexes was also observed. In the acyclic complexes both the terminal OH groups make a bifurcated hydrogen bond, a donor formed hydrogen bondings with more than one acceptor simultaneously [25]. Obviously, there is no bifurcated hydrogen bond in the cyclic complexes, due to no OH terminal group in the ligand. Generally, the acyclic complexes have five hydrogen bonds, namely, two pairs of $C–H\cdots O_{nitro}$ hydrogen bonds from oxygen atom in two nitro functional groups of monodentate picrate and $O–H\cdots O$ from the terminal groups in the acyclic EO5 ligand. Thus, the complexes are stabilized by two moderate and three weak hydrogen bonds [26] (Table 2).

A third picrate has also played a significant role in the stability of the acyclic complexes, as can be seen in (Figure 3b) for **(b)** a long contact of $Eu–O_{phenolic}$ between oxygen atom from the third picrate and Eu^{3+} at the distance of 4.252 Å was observed. This weak interaction was facilitated by the position of $O_{phenolic}$ in the third picrate anion which is directly planar to the Eu(III) ion. Nevertheless, no contact between $Nd–O_{phenolic}$ in the third picrate due to the position is out of plane two atoms. In contrast to the cyclic complexes, **(c)** and **(d)** only one-type of intermolecular C–H···O hydrogen bonds from $O_{acceptor}$ of nitro the third picrate was formed (Figure 4). The weak hydrogen bonds in **(c)** and **(d)** complexes are similar as shown in C(7A)–H(7AA)···O(27A)–N(9A) 2.570 Å (106.9°). Hydrogen bond that occur from the interaction the first two picrate molecules, namely C(2B)–H(2BB)··· O(27A)–N(9A) [2.551 Å (136.0°)] is shorter than from the third free picrate anion. In addition to the hydrogen bonding as discussed above, the acyclic complexes are also shown to have a close contact between N–O_{nitro}··· O_{nitro} from oxygen atoms of the third picrate and bidentate picrate. The observed distances of N–O···O in the **(c)** and **(d)** complexes are 2.885 Å (134.4°) and 2.921 Å (126.6°), respectively. The $O_{phenolic}$ from the third picrate in the cyclic complexes does not contribute to the formation of the hydrogen bonding by virtue of the position the phenolic is quite a distance relative to the oxygen atoms of nitro groups and furthermore its position is not planar.

Conclusion

18-crown-6 and pentaethylene glycol are suitable ligands to form a stable cyclic complexes. The rigid cyclic ligand 18-crown-6 with fixed cavity is expected to form a complex with rigid structure. Pentaethylene glycol used all six oxygen donor atom to form hexadentate "cyclic-like" conformation of the complexes. Maintaining its flexibility, EO5 exhibits a stable conformation with better opportunity of forming hydrogen bonding to contribute to more stable complex relative to the cyclic ligand. The picrate anion has shown a remarkable ability to form bonding thus a suitable choice as counter anion to neutralize and stabilize of the complexes.

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List Tables

Table 1 Crystallographic data for the acyclic and the cyclic complexes

Parameter	Nd acyclic **(a)**	Eu acyclic **(b)**	Nd cyclic **(c)**	Eu cyclic **(d)**
Empirical Formula	$C_{28}H_{28}NdN_9O_{27}$	$C_{28}H_{28}$ Eu N_9O_{27}	C_{30} H_{30} Nd N_9 O_{27}	C_{30} H_{30} Eu N_9 O_{27}
Coordination Numbers	9	9	10	10
Formula Weight	1066.82	1074.55	1082.86	1100.59
Temperature	293 K	293 K	293 K	293 K
Melting point	263.8 °C	257.1 °C	289°C	278°C
Volume (Å^3)	3860.24(8)	3838.4(3)	7804.9 (19)	7827.4(19)
Z	4	4	8	8
Crystal System	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space Group	$P2_1/c$	$P2_1/c$	*Pbca*	*Pbca*
Unit cell dimensions	a=18.7757(7) Å b = 9.03370(10) Å c = 24.0936(3) Å α=γ=90°, β=109.160(1)°	a=18.7409(7) Å b = 9.0098(4) Å c = 24.0692(10) Å α=γ=90°, β=109.184(1)°	a = 11.0675(16) Å b =23.607(3) Å c = 29.873(4) Å α= β = γ = 90°	a = 11.0639(16) Å b = 23.532(3) Å c =30.064(4)Å α= β = γ = 90°
Density	1.836 mg/m^3	1.859 mg/m^3	1.860 mg/m^3	1.868 mg/m^3
Absorption coefficient	1.460 mm^{-1}	1.750 mm^{-1}	1.447 mm^{-1}	1.719 mm^{-1}
Limiting indeces	$-26 \leq h \leq 26$ $-12 \leq k \leq 12$ $-33 \leq l \leq 33$	$-14 \leq h \leq 25$ $-11 \leq k \leq 12$ $-31 \leq l \leq 30$	$-13 \leq h \leq 14$ $-30 \leq k \leq 27$ $-38 \leq l \leq 38$	$-14 \leq h \leq 14$ $-30 \leq k \leq 24$ $-38 \leq l \leq 39$
F(000)	2140	2152	4392	4416
Theta range for data collection (°)	1.15 – 30.03	2.43 – 28.33	1.36-27.63	1.35 - 27.64
Independent reflection Data/parameter	8192/586	9437 / 596	72019 / 9022	50776 / 9074
R(int)	0.0288	0.0175	0.0313	0.0300
Goodness-of-fit on F2	1.073	1.058	1.069	1.296
Final R indeces [$I > 2\sigma(I)$]	R = 0.0435, wR = 0.1224	R = 0.0301, wR = 0.0769	R = 0.0328, wR = 0.0857	R = 0.0530, wR = 0.1069

Table 2 Selected bond lengths (Å) for the acyclic {$[Ln.(pic)_2.EO5]^+[pic]^-$} and the cyclic {$[Ln.(pic)_2.18C6]^+[pic]^-$} complexes

Bond	Length (Å)			
	Nd acyclic	Eu acyclic	Nd cyclic	Eu cyclic
Ln(1)– O(1)	2.571(3)	2.459(2)	2.513 (2)	2.487 (3)
Ln(1) –O(2)	2.565(3)	2.497(19)	2.510 (2)	2.597 (3)
Ln(1) –O(3)	2.494(3)	2.546(2)	2.606 (2)	2.537 (3)
Ln(1) –O(4)	2.496(3)	2.465(2)	2.565 (2)	2.552 (4)
Ln(1) –O(5)	2.541(3)	2.523(2)	2.574 (2)	2.495 (3)
Ln(1) –O(6)	2.575(3)	2.539(2)	2.533 (2)	2.482 (3)
Ln(1) –O(7)	2.356(3)	2.307(3)	2.374 (2)	2.327 (3)
Ln(1) –O(8)	2.564(3)	2.504(2)	2.576 (2)	2.541 (3)
Ln(1) –O(14)	2.349 (3)	2.307(3)	2.341 (2)	2.270 (4)
Ln(1) –O(15)	-	-	2.744 (3)	2.942 (6)
Hydrogen bond				
C(7) –H...O(27)	2.443	2.440	2.570	2.570
C(13) –H...O(22)	2.349	2.356	-	
O(15) –H...O(27)	2.353	2.386	-	-
O(15) –H...O(21)	1.849	1.856	-	-
O(20) –H...O(21)	1.998	1.999	-	-

Note: Please refer to Figure 3a for the atom numbering (all complexes take the same numbering)

Table 3 Selected bond angles (°) in the acyclic and the cyclic complexes

Bond	Angles (°)			
	Nd acyclic **(a)**	Eu acyclic **(b)**	Nd cyclic **(c)**	Eu cyclic **(d)**
O(1)-Ln(1)-O(2)	**71.63(10)**	**71.87(7)**	64.44(7)	62.03(11)
O(2)-Ln(1)-O(3)	62.28(11)	63.27(6)	61.95(7)	62.77(11)
O(3)-Ln(1)-O(4)	61.84(13)	61.43(7)	62.42(7)	63.41(12)
O(4)-Ln(1)-O(5)	62.66(12)	62.70(8)	63.04(8)	62.54(12)
O(5)-Ln(1)-O(6)	60.89(10)	62.42(9)	62.39(8)	62.47(12)
O(6)-Ln(1)-O(1)	62.76(9)	62.67(8)	62.00(8)	64.93(11)
O(7)-Ln(1)-O(8)	66.19(10)	67.59(7)	63.61(7)	64.83(11)
O(14)-Ln(1)-O(15)	-	-	61.89(8)	59.52(15)

Note: Please refer to Figure 3a for the atom numbering (all complexes take the same numbering). Bold type show to the terminal OH groups.

Figure Caption

Figure 1 IR spectra (KBr pellets) of the cyclic and acyclic complexes. A = 18C6 and B = EO5 (Pentaethylene glycol) and C = Picric acid

Figure 2 Comparison on the thermogram of (**a** = green, **b** = red, **c** = blue and **d** = pink) complexes

Figure 3a To show hexadentate of the cyclic ligand (18C6) by probability 50 % **(d)**; Figure 3b To show the interaction between Eu$\cdots$O$_{\text{phenolic}}$ (4.252 Å) which an exotic behavior of **(b)** complex by probability 50 %.

Figure 4 The ORTEP **(c)** to show two bidentate, solvated picrate and intermolecular C–H$\cdots$O hydrogen bonds by axis c.

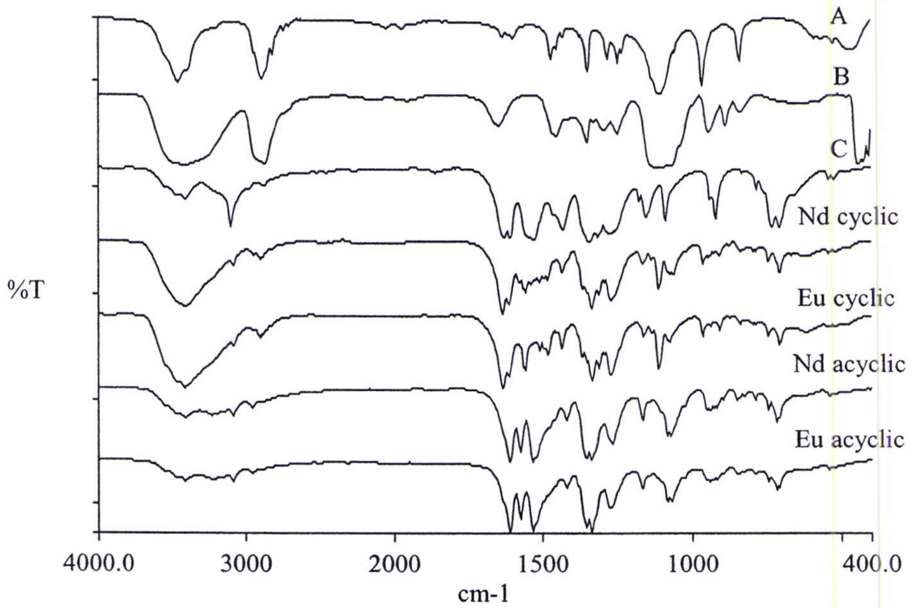
A
B
C
Nd cyclic
Eu cyclic
Nd acyclic
Eu acyclic
%T
4000.0
3000
2000
1500
1000
400.0
cm-1

Figure 1

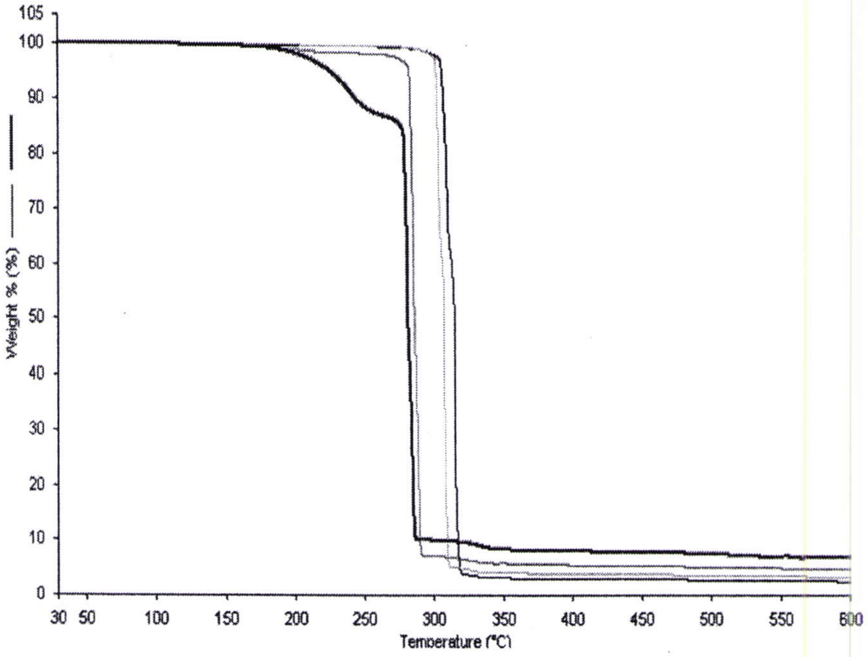
105
100
90
80
70
60
50
40
30
20
10
0
Weight % (%)
30
50
100
150
200
250
300
350
400
450
500
550
600
Temperature (°C)

Figure 2

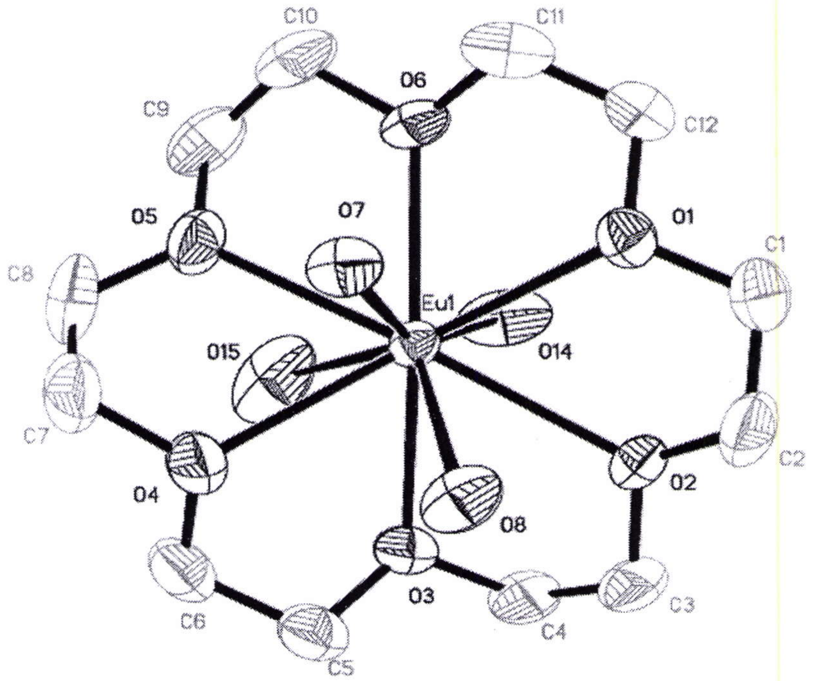

Figure 3a

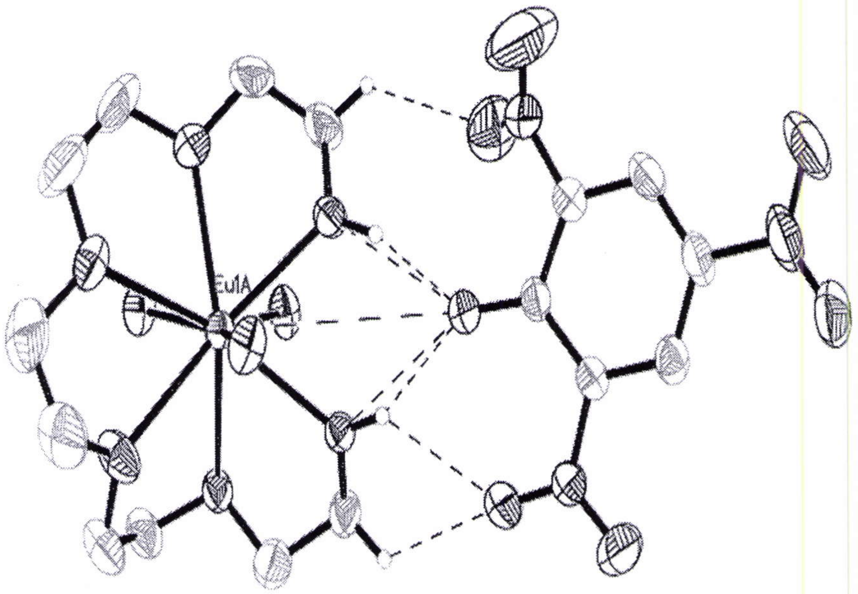

Figure 3b

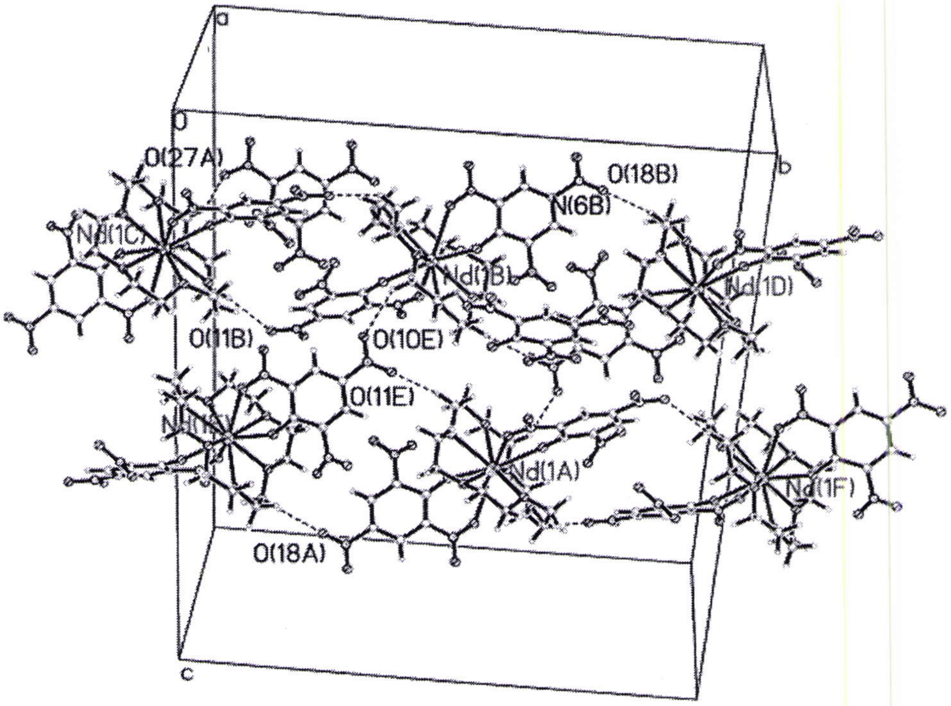
a
0
b
c
O(27A)
O(18B)
N(6B)
Nd(1C)
Nd(1B)
Nd(1D)
O(11B)
O(10E)
O(11E)
Nd(1A)
Nd(1F)
O(18A)

Figure 4

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SIMULTANEOUS SOLVENT EXTRACTION OF METAL IONS WITH THIACROWN ETHERS STUDIED USING INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

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Abstract

Simultaneous solvent extraction of ten metal ions (Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}) with three thiacrown ethers, namely 1,4,7,10-tetrathiacyclododecane (12S4), 1,4,7,10,13-pentathiacyclopentadecane (15S5) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) in 1,2-dichloroethane was studied using inductively coupled plasma-mass spectrometry (ICP-MS). Picric acid was used as counter ion. Key extraction parameters such as contact time, pH, ligand and counter ion concentrations were investigated. The three thiacrown ethers show high selectivity towards Ag^{+}, followed by Hg^{2+} and Cu^{2+} over the other metal ions studied. Under the optimized conditions, 10 ppm Ag^{2+} was selectively extracted from 1×10^{-3} M picric acid at pH 5 for 12S4, pH 4 for 15S5 and 18S6 into 1,2-dichloroethane containing 2×10^{-4} M ligand. This procedure was applicable to the selective extraction and determination of Ag^{+} from river water sample. The stoichiometries of the extracted complex is also established.

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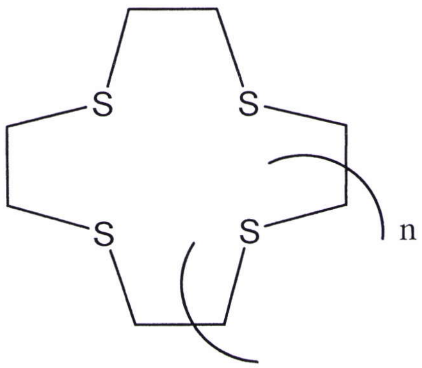
Introduction

Solvent extraction, in conjunction with suitable ligands, has been widely used for the pre-concentration and separation of metal ions. Among the various ligands useful for metal ion complexation are the crown ethers and their analogues[1]. Crown ethers have been extensively investigated and are known to be effective for the extraction of hard and soft metal ions with the assistance of an appropriate counter anion[2]. Thiacrown ethers are a class of crown ethers where the donor oxygen atoms on the macrocyclic ring are partially or totally replaced by sulphur atoms. Thiacrown ethers are classified as a soft Lewis bases and are well-known to interact selectively with soft Lewis acids.

Accordingly, most of the past research efforts has focused on thiacrown ether complexation with soft or borderline metal ions[3], such as Cu^+, Cu^{2+}, Ag^+ and Hg^{2+} [4,5]. Several excellent review articles dealing with the coordination chemistry of 12 to 16-membered thiacrown ethers have been published[6,7]. Sevdic *et al.*[4,5] studied the complex formation properties of thiacrown ethers containing four, six and eight sulphur donor atoms with Ag^+ and Hg^{2+}, picrate and perchlorate serving as counter ions. Complexes of the ratio (metal : ligand) 1 : 1 and 2 : 1 for Hg^{2+} and 1 : 1, 2 : 1 and 3 : 1 for Ag^+ with six sulphur ligand, 1 : 1 for Hg^{2+} and 1 : 1 and 2 : 1 for Ag^+ with four sulphur ligand had also been reported. Ring size effect on the structure of the crown complex has also been discussed. It is further noted that Ag^+ form the most stable complexes with the six-membered sulphur ligand over the eight and four ones. Solid state complexes of Ni^{2+}, Co^{2+} and third state metal ions such as Cr^{3+}, Co^{3+} and Fe^{3+} with thiacrown ethers (9S3, 10S3, 12S3, 18S6, 24S6) were also reported[8-12]. Due to their excellent selectivity, they readily lend themselves as useful analytical reagents for the determination of Hg^{2+}, Ag^+ and Cu^{2+} [3, 13-14]. Accordingly, extraction of these metal ions with thiacrown ethers have been studied much more widely than extraction with other types of crown ethers[15-17]. Saito *et al.*[3,18], extensively studied the extraction behaviour of Cu^{2+} with 12 to 16-membered tetrathiacrown ether using tetraphenylborate (TPB) or picrate (Pic) as counter ions. The use of a few thiaethers as chemical sensors have also been reported[19,20].

Since the introduction of the first commercial instrument in 1983[21], inductively coupled plasma-mass spectrometry (ICP-MS) has gained prominence as a powerful technique for elemental analysis. ICP-MS offers rapid and simultaneous multi-element analysis, with detection limits ranging from parts per billion to parts per trillion. Other unique capabilities of ICP-MS include, relatively simple spectra and the ability to conduct isotopic analysis[22,23]. ICP-MS has currently become a universally accepted analytical technique for multi-element determination in diverse fields such as environmental[24], geological[25,26], industrial[27], biological and clinical[28,29].

It should be pointed out that, in all previous reports on the extraction using thiacrown ethers, only one metal ion was studied at a time. In the present work, however, the ICP-MS is applied for the determination of several metal ions (Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}) after their simultaneous solvent extraction with three cyclic thiacrown ethers namely 1,4,7,10-tetrathiacyclododecane **(12S4)**, 1,4,7,10,13-pentathiacyclopentadecane **(15S5)** and 1,4,7,10,13,16-hexathiacylooctadecane **(18S6)** **(Figure 1)**. Picric acid was used as counter anion. Factors that contribute to the extraction in the studied system such as contact time, the concentration of H^+, ligand and counter ion concentrations and selectivity amongst the metal ions are investigated.



n=1, 12S4
n=2, 15S5
n=3, 18S6

Fig. 1. Chemical structure of thiacrown ethers studied

Experimental

Apparatus

A Perkin Elmer Elan 6100 inductively coupled plasma-mass spectrometry (ICP-MS) with version 2.0 software was used in the studies. The instrument conditions and general method parameters are listed in **Table 1**. An Orion Ion Analyzer model EA940 was used for pH measurements. A mechanical shaker (Stuart Scientific, UK) was used for extraction. De-ionized water was produced from Millipore Milli-Q plus.

Table 1: ICP-MS instrumental operating conditions and data acquisition parameters

Condition / parameters	Result
ICP parameters	
R.f. power (W)	1000
Coolant argon flow rate (L min^{-1})	15
Auxiliary argon flow rate (L min^{-1})	1
Nebulizer argon flow rate (L min^{-1})	97
Operating frequency (MHz)	40
Sample introduction system	Cross flow nebulizer
Sample cone	Nickel with a 1.1 mm orifice
Skimmer cone	Nickel with a 0.9 mm orifice
Scanning mode	Peak hopping
Pressure (quadrupole analyzer) ICP (Torr)	$4.18 X 10^{-5}$
Number of replicate	2

Chemical and Reagents

Stock solution (100 ppm) containing mixture of metals (sulfates of Zn^{2+}, Cd^{2+}, V^{4+}, Ni^{2+}, Cu^{2+}, Mn^{2+}; nitrates of Mg^{2+}, Co^{2+}, Ag^{+} and chloride of Hg^{2+} in a final volume of 250 mL were prepared by dissolving appropriate amount of metal salt in 2% HNO_3 solution.

Thiacrown ethers, 12S4, 15S5 and 18S6 (Aldrich) were used without further purification. Appropriate amount (0.01 M) of the thiacrown ether were dissolved in 1,2-dichloroethane (Merck).

A standard solution (0.01 M) of picric acid (BDH) was prepared by dissolving 0.229 g of the dried acid in 100 mL of de-ionized water. A 1 M sodium acetate (Riedel-deHaen) solution was prepared by dissolving 34.02 g of the salt in 250 mL de-ionized water.

For the determination of Ag^+ in real sample, river water was collected from Waterfall River, Penang, Malaysia. The water was filtered to remove suspended particles.

Liquid-Liquid Extraction

An aliquot sample solution (5 mL) containing a mixture of metal ions (10 ppm each) and picric acid (1×10^{-3} M) was placed in 100 mL stoppered conical flask. The pH was adjusted to the desired value with sodium acetate (1 M). An organic solution (5 mL) containing

2×10^{-4} M thiacrown ether in 1,2-dichloroethane was added. The mixture was shaken mechanically for 45 min at room temperature. After shaking, the phases were allowed to settle, separate and metal ions concentration left in the aqueous phase was determined using ICP-MS. The amount of the metal ion extracted into the organic phase was determined by difference.

Distribution Equilibrium of Metal Ion

The distribution equilibrium of metal ion (M^{n+}) from an aqueous picrate (Pic^-) medium with thiacrown ether (L) in the present system can be described in general according to *Eq*. (**1**). The extraction constant, K_{ex} is defined by *Eq*. (**2**).

$$M^{n+} \quad + \quad mPic^{-} \quad + \quad n(L)_{org} \rightleftharpoons [MPic_m(L)_n]_{org} \quad \text{-------} \; \mathbf{(1)}$$

$$K_{ex} = [MPic_m(L)_n]_{org} / [M^{n+}][Pic^{-}]^m[L]^n_{org} \quad \text{--------------------------} \; \mathbf{(2)}$$

The distribution ratio (D) can be calculated as in *Eq.* (**3**).

$$D = [M^{n+}]_{org} \;/\; [M^{n+}] \;=\; K_{ex}[Pic^{-}]^m[L]^n_{org} \quad \text{--------------------------} \; \mathbf{(3)}$$

Where $D = [MPic_m(L)_n]_{org} / [M^{n+}]$

$$\mathrm{Log}D = \mathrm{Log}\, K_{ex} \;+\; m\,\mathrm{Log}[Pic^{-}] \;+\; n\,\mathrm{Log}[L]_{org} \quad \text{-------------------} \; \mathbf{(4)}$$

In the presence of two species (M_1Pic_m) and (M_2Pic_m) in the aqueous phase (where M_1 and M_2 refer to different species of metal ions), then the distribution ratio can be written as

$$D = [MPic_mL_n]_{org} \;/\; [M_1Pic_m] + [M_2Pic_m] \quad \text{------------------------} \; \mathbf{(5)}$$

The selectivity (β) among the species can be related to the relative extraction constant K_{ex1} and K_{ex2} is given by *Eq.* **6** [30].

$$\beta = K_{ex2} \;/\; K_{ex1} = D_2 \;/\; D_1 \quad \text{---------------------------------} \; \mathbf{(6)}$$

Results and Discussion

Effect of Contact Time

The solution was shaken on a mechanical shaker from 5 to 45 min. Results show that all the thiacrown ethers undergo a maximum extraction for Ag^+ (**Fig. 2**) after shaking for 10 min or longer, followed by Hg^{2+} and Cu^{2+}. However, once the maximum extraction has reached, increasing of contact time has no significant effect on the extraction. Therefore, an equilibrium time of 45 min was adopted for subsequent extraction studies to ensure complete extraction. This period of time was also found to be the best by Ikeda and Abe[31] on their solvent extraction of Cu^{2+} with tetrathiacrown ether derivative.

Effect of pH

The effect of pH on the metal extraction by the three ligands is summarized in **Figure 3**. The degree of extraction is found to increase with pH for Ag^+, Hg^{2+} and Cu^{2+} when 12S4 is used as extractant. A similar trend in pH extraction profile is exhibited for Hg^{2+} and Cu^{2+} when 15S5 and 18S6 are used as extractants, reflecting that the thiacrown ether's extraction efficiency for Hg^{2+} and Cu^{2+} are highly dependant on the ionization of picric acid in the medium. Therefore, pH 5 is the optimum pH for the extraction of Hg^{2+} and Cu^{2+} with 12S4, and pH 4 is the best for 15S5 and 18S6 systems. The percentage of extraction slightly decreases at pH lower or higher than the optimum pH for the extraction of Hg^{2+} and Cu^{2+} in all the studied systems. This pH profile agree well with the findings of Saito *et al.*[18] on their solvent extraction of Cu^{2+} with 12S4 but do not agree well with the findings of Ikeda and Abe[31], were Cu^{2+} can be extracted quantitatively (100 %E) at pH above 6 when extracted with 12S4 derivative.

No noticeable effect of pH on the extraction of Ag^+ with 15S5 and 18S6 was observed. A little acceptance at the acidic medium (pH 2) on the extraction of Ag^+ with 12S4 was observed (**Fig 2A**). However, increasing the pH of the aqueous solution enhances the formation of the complex, which reaches a maximum at pH ~ 4. These findings are a reflection of the independence of Ag^+ on the ionization of the counter anion on its complexation with 12S4. Therefore, pH 5 for 12S4 and pH 4 for 15S5 and 18S6 are used in subsequent work.

The %E values for the other metal ions, (Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) are below 8% (Log D < -1) for both 12S4 and 15S5 and slightly more than 15% (Log D < -0.8) for 18S6. This implies that these metal ions were very poor extracted under the studied conditions. Therefore, due to the favourable extraction characteristics of these ligands towards Ag^+, Hg^{2+} and Cu^{2+}, no further experiments are carried out involving the other metal ions.

Effect of Ligand Concentration

The influence of 12S4, 15S5 and 18S6 concentration was studied by extracting the metal ions with different amount of ligands, varied from 2×10^{-5} to 6×10^{-4} M. The extraction was carried out at the respective optimum pH (5 for 12S4 and 4 for both 15S5 and 18S6). Overall results show that the extraction was optimum when the ligand concentration $\geq 2 \times 10^{-4}$ M. **Figure 4** shows the effect of 12S4, 15S5 and 18S6 concentration on the distribution ratio (Log D) for Ag^+, Hg^{2+} and Cu^{2+} using 1×10^{-3} M picrate concentration. A good linear dependence on ligand concentration with a normal slopes of 0.5 for Ag^+ and Hg^{2+}, 2 for Cu^{2+} with 12S4, 1.5 for Ag^+, 2 for Hg^{2+}, 1.4 for Cu^{2+} with 15S5 and 1.5 for Ag^+, 0.4 for Hg^{2+} and 1.0 for Cu^{2+} with 18S6. This dependence confirms the general applicability of Eq. 3 in describing the extraction process. These results indicated that ligand 12S4 form complexes of ratios of 1:2 with Ag^+ and Hg^{2+} and 2:1 with

Cu^{2+}, ligand 15S5 form complexes of ratios of 3:2 with Ag^{+} and Cu^{2+} and 2:1 with Hg^{2+}, and ligand 18S6 form complexes of ratios of 3:2 with Ag^{+}, 1:2 with Hg^{2+} and 1:1 with Cu^{2+} in the presence of picrate anion. Therefore, 2×10^{-4} M of thiacrown ethers was adopted as a suitable concentration for subsequent extraction study.

Effect of Picrate Concentration

A study of picrate ion concentration varied from 5×10^{-5} to 1.4×10^{-3} M was examined under constant ligand concentration (2×10^{-4} M) and pH 5 for 12S4 and pH 4 for both 15S5 and 18S6. **Figure 5** shows the effect of picrate concentration on the distribution ratios of Ag^{+}, Hg^{2+} and Cu^{2+}. The log D values linearly increase with increase in the picrate concentration for all cases. The slopes of the logarithmic plot of D vs. picrate concentration were found equal to 0.5 for Ag^{+}, 0.4 Hg^{2+} and 1 for Cu^{2+} with 12S4, 0.7 for Ag^{+}, 0.2 for Hg^{2+} and 0.5 for Cu^{2+} with 15S5 and 1.5 for Ag^{+}, 0.4 for Hg^{2+} and 0.6 for Cu^{2+} with 18S6. These results indicate that two mole picrate is associated with Ag^{+} and Hg^{2+} ions while one moles for Cu^{2+} when extracted with 12S4 from picrate medium. However, 0.7 moles of picrate are needed for the extraction of one mole Ag^{+} with both 15S5 and 1.5 for 18S6 ligands, while 0.5 mole of picrate is necessary for the extraction of Cu^{2+} with 15S5 and 0.4 mole of picrate is needed for the extraction of Hg^{2+} with 18S6.

Separation

Under the optimum extraction system of 2×10^{-4} M ligand and 1×10^{-3} M picrate as a counter anion, the percentage extraction (%E) of the studied metal ions with 12S4, 15S5 and 18S6 is in the order $Ag^{+} >> Hg^{2+} > Cu^{2+}$, $Ag^{+} >> Cu^{2+} > Hg^{2+}$ and $Ag^{+} >> Hg^{2+} > Cu^{2+}$ respectively. The separation factor of metal ions are summarized in Table 2. The table shows that all the thiacrown ethers are very selective towards Ag^{+}.

Table 2: Separation factor (β) of metal ions by different ligands

Metal	β		
	12S4	15S5	18S6
Ag / Hg	16.93	8.32×10^3	256.88
Ag / Cu	1.78×10^3	135.32	460.96
Hg / Ag	5.90×10^{-2}	1.20×10^{-4}	3.89×10^{-3}
Hg / Cu	105.26	1.60×10^{-2}	1.79
Cu / Ag	5.61×10^{-4}	7.39×10^{-3}	2.17×10^{-3}
Cu / Hg	9.50×10^{-3}	16.48	0.56

These results further show that 15S5 is the best ligand for the extraction and separation of Ag^+ or Cu^{2+} in the presence of Hg^{2+} ($\beta = 8.32 \times 10^3$ and 16.48 respectively), while 12S4 was found to be the best ligand for a selective separation of Ag^+ or Hg^{2+} in the presence of Cu^{2+} ($\beta = 1.78 \times 10^3$ and 105.26 respectively). Poor selectivity of 18S6 among Hg^{2+} and Cu^{2+} have also been observed.

Determination of Ag^+ in river water sample

The determination of Ag^+ in a river water sample was conducted using the proposed extraction procedure. Firstly, the water was directly analyzed with ICP-MS to determine the metal ions content. The main metal ions found in the river water are Mg^{2+} (194 ppb), Zn^{2+} (3 ppb), Mn^{2+} (2 ppb) and Ca^{2+} (2001 ppb), but Ag^+ was not detected in the sample. The data are average of three determinations mainly carried out from different spots. Next, various concentration of Ag^+ (5, 10, 20, 40 ppm) was spiked respectively to the samples. The extraction results of these spiked samples are summarized in Table 3.

Overall results proved that all of the three thiacrown ethers show significant extraction (> 90%) of Ag^+ in the river water sample. Up to 10 ppm of Ag^+ was extracted quantitatively (100% E) by 15S5 and 18S6. However, the percentage of extraction slightly decreased when the spiked Ag^+ level was increased.

Table 3: %E of Ag^+ from spiked river water sample

Ag^+ spiked (ppm)	%E		
	12S5	15S5	18S6
5	95.8 (0.5)	100 (0.1)	100 (0.1)
10	93.8 (0.8)	100 (0.1)	100 (0.1)
20	91.4 (0.3)	98.0 (0.3)	98.7 (0.3)
40	90.2 (0.6)	97.7 (0.5)	97.8 (0.9)

* n = 3

Conclusion

A simultaneous solvent extraction system having excellent selectivity towards Ag^+ has been developed using the thiacrown ethers (12S4, 15S5 and 18S6) as macrocyclic neutral ligands and picrate as counter anion. The selectivity trend of these ligands are found to be the best for Ag^+, followed by Hg^{2+} and Cu^{2+}. However, negligible extraction was observed for other studied metal ions. On the whole, the results obtained are in agreement with those obtained by single-element analysis but we believe the present approach give more realistic information about the selectivity behaviour of these kind of macrocyclic ligands towards metal ions in a mixture. This extraction-ICP-MS method was successfully applied for the separation of Ag^+ in river water sample. The immobilization of these ligands for analytical applications under batch and flow conditions are actively being persued in our laboratories.

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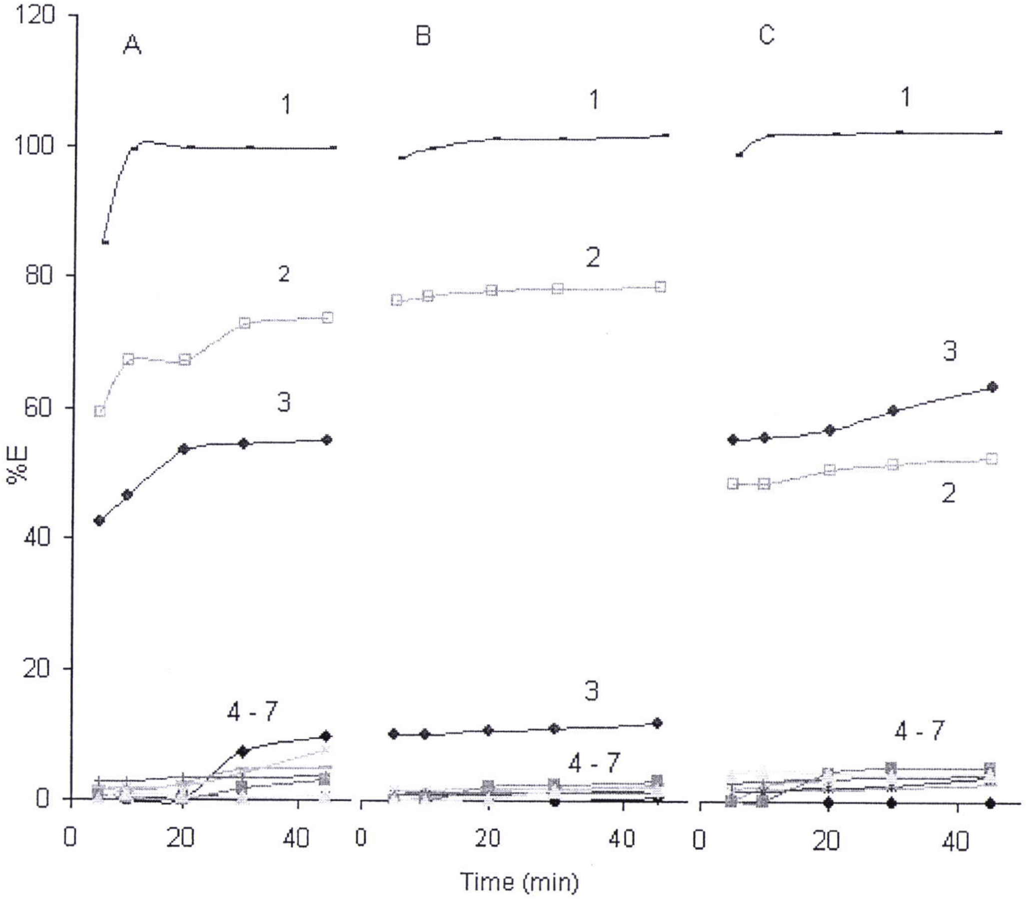

Fig.2. Effect of equilibrium time on the extraction of metal ions (1= Ag^+, 2= Hg^{2+}, 3= Cu^{2+}, 4-7= Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) with 2×10^{-4} M thiacrown ether (A= 12S4, B= 15S5, C= 18S6). Picrate concentration 1×10^{-3} M.

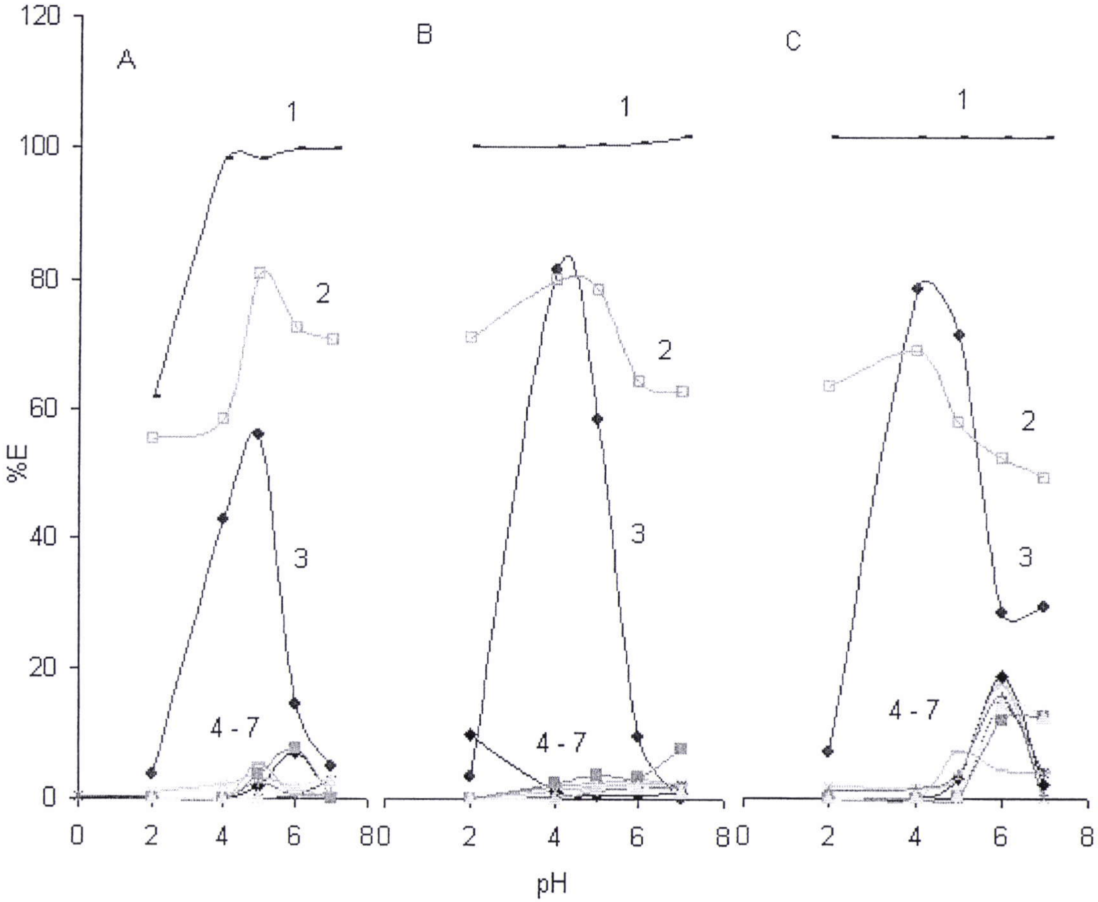

Fig.3. Effect of pH on the extraction of metal ions (1= Ag^+, 2= Hg^{2+}, 3= Cu^{2+}, 4-7= Mg^{2+}, V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) with 2×10^{-4} M thiacrown ether (A= 12S4, B= 15S5, C= 18S6). Picrate concentration 1×10^{-3} M.

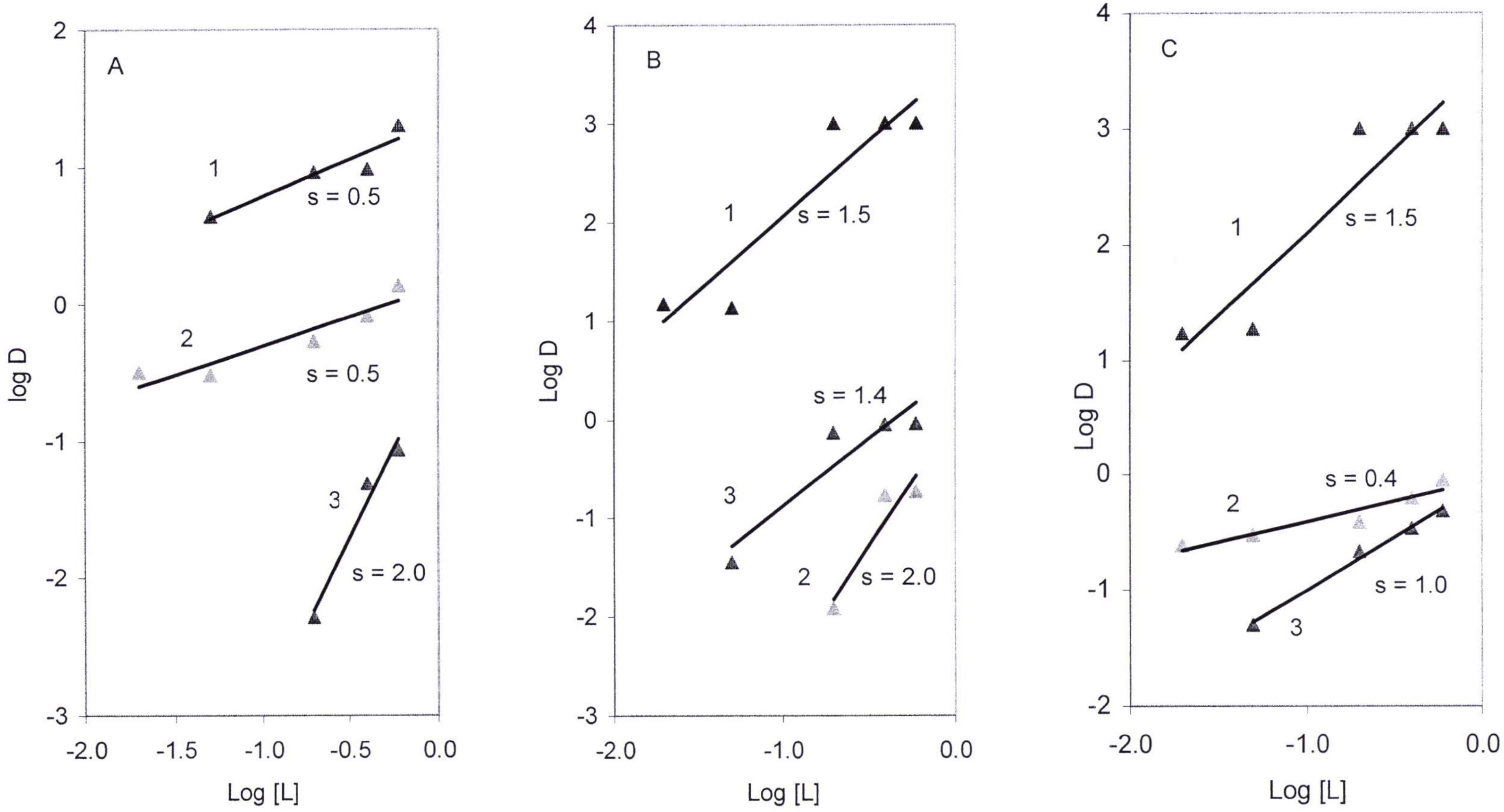

Fig.4. Effect of thiacrown ether (A= 12S4, B= 15S5, C= 18S6) concentration on the distribution ratio of metal ions

(1= Ag^+, 2= Hg^{2+}, 3= Cu^{2+}) from picrate medium (1×10^{-3} M), pH (A= 5, B & C= 4), s= slope.

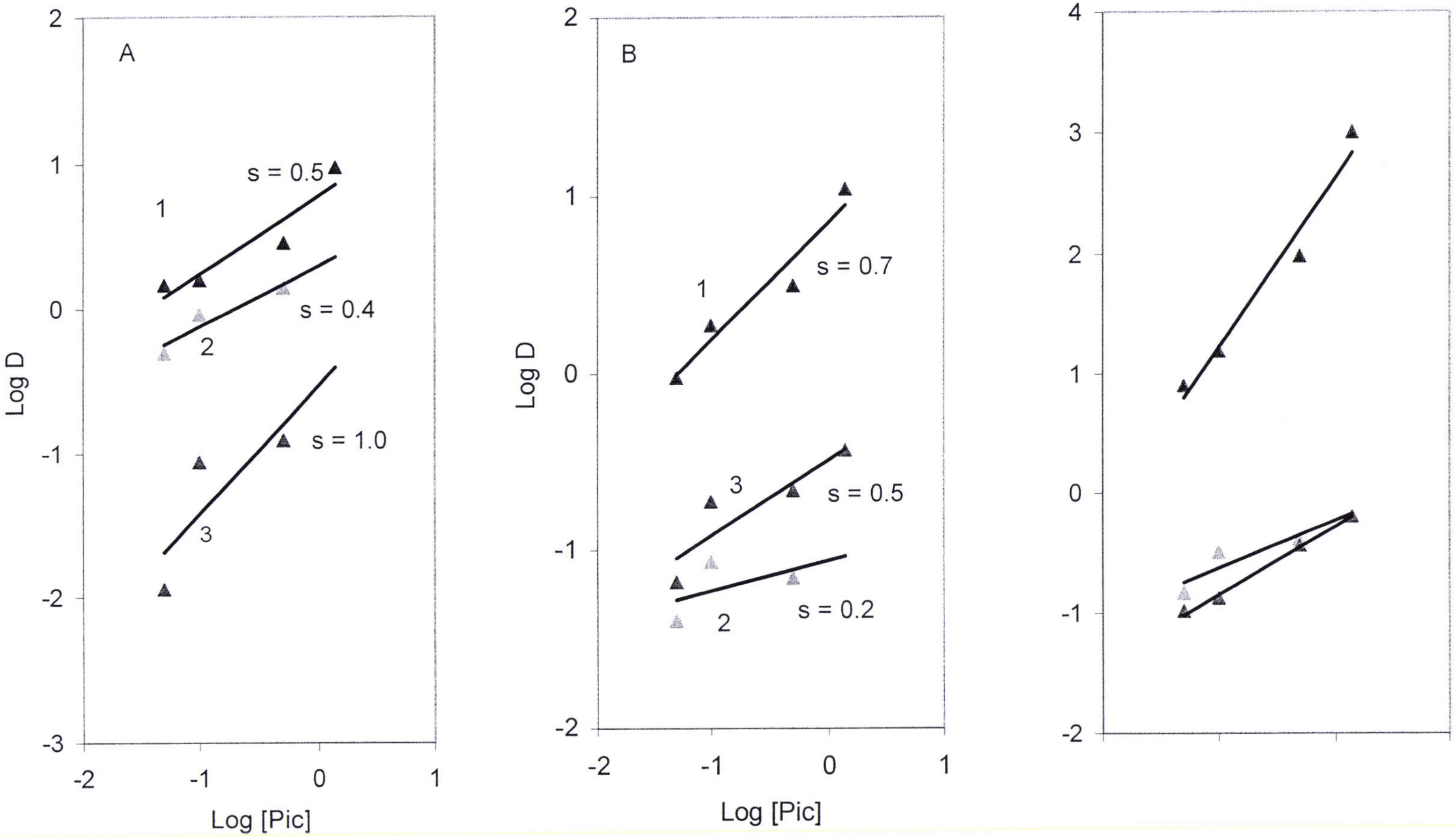

Fig.5. Effect of picric acid concentration on the distribution ratio of metal ions (1= Ag^+, 2= Hg^{2+}, 3= Cu^{2+}) with (2×10^{-4} M) thiacrown ether (A= 12S4, B= 15S5, C= 18S6), pH (A= 5, B & C= 4), s= slope.