

Syntheses, spectroscopic characterization and metal ion binding properties of benzo-15-crown-5 derivatives and their sodium and nickel(II) complexes

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Abstract New benzo-15-crown-5 derivatives containing nitro, amine and imine groups were prepared. Nitro compound (**1**) was prepared after the reaction 4',5'-bis(bromethyl)benzo-15-crown-5 and *o*-nitrophenol in the presence of NaOH. After reduction process by using hydrazine hydrate and Pd/C amine compound (**2**) was formed. New crown ether imine compounds (**3–5**) were synthesized by the condensation of corresponding crown ether diamine (**2**) with salicylaldehyde derivatives. Sodium complexes of the crown compounds (**1a–5a**) form crystalline 1:1 (Na⁺:ligand) complexes with sodium perchlorate. Nickel(II) complexes (**3b–5b**) with 1:1 (Ni²⁺:ligand) stoichiometries were also been synthesized from the Schiff bases (**3–5**). The results indicated that the Schiff base ligands coordinated through the azomethine nitrogen and phenolic oxygen. The extraction ability of compounds (**1**, **3**, **4** and **5**) were also evaluated in chloroform by using several alkali and transition metal picrates such as Li⁺, Na⁺, K⁺, Cr³⁺, Mn²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Pb²⁺.

Keywords Crown ethers · Solvent extraction · Imine compounds · Nickel(II) complexes · NMR spectroscopy · Sodium complexes

Introduction

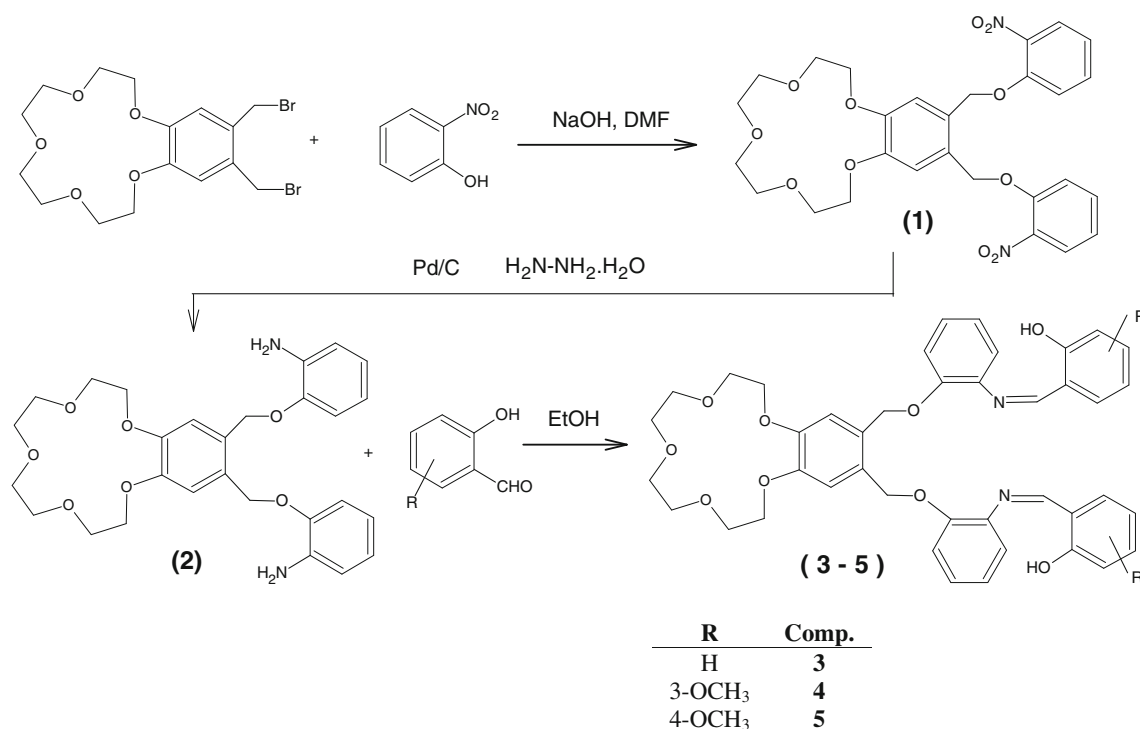
Since the pioneering publication of Pedersen in 1967 extensive research has been devoted to the preparation and study of the properties of macrocyclic polyethers [1–4].

This enormous growth has been due to the synthesis of a great number and variety of synthetic macrocyclics that have behave as coordinating agents for alkali and alkaline earth metal ions. Crown ethers have attracted great interest in the last three decades, not only from the synthetic and selectivity alkaline and alkaline earth metal cation complexation properties point of view, but also with respect to their unusual structural characteristics [5]. Crown and benzo-crown compounds with additional donor atom(s) or functional group(s) have been synthesized in order to alter the cation binding ability and selectivity of the parent crown ethers through further fixing of the side arm donor to a cation benefited in the crown ether cavity.

Benzo condensed crown compounds having reactive nitro or amine substituent at the aromatic ring are considered as an interesting starting materials for the synthesis of new molecules [3, 4]. Crown ether Schiff base ligands are important molecules extensively studied with respect to their high affinity to interact with alkali and transition metal ions [6–9]. In general, oxygen crown ether rings are effective for the complexes of alkali and alkaline earth metal cations but not transition metal cations. Conversely, their Schiff base structure with salicylidene modify benzocrown ethers are effective for transition metal ions but not alkali metal cations [10]. So, salicylidene crown ether containing Schiff bases are known to bind cations in the crown ether cavity in addition to the coordination of a transition metal center through the N₂O₂ donor atoms [11].

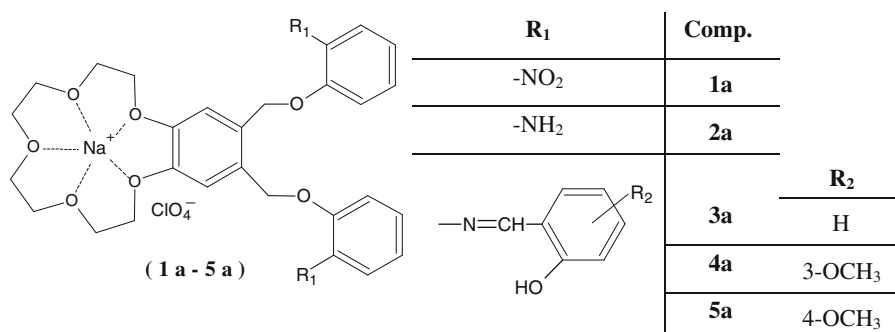
The aim of this study is to developing a series of new crown ether compounds (**1–5**), alkali (**1a–5a**) and transition metal complexes (**3b–5b**). The way of the synthesis of crown ether nitro (**1**), amine compound (**2**), Schiff base ligands (**3–5**) and their sodium (**1a–5a**) and nickel(II) (**3b–5b**) complexes are shown in Schemes 1, 2, and 3. Solid

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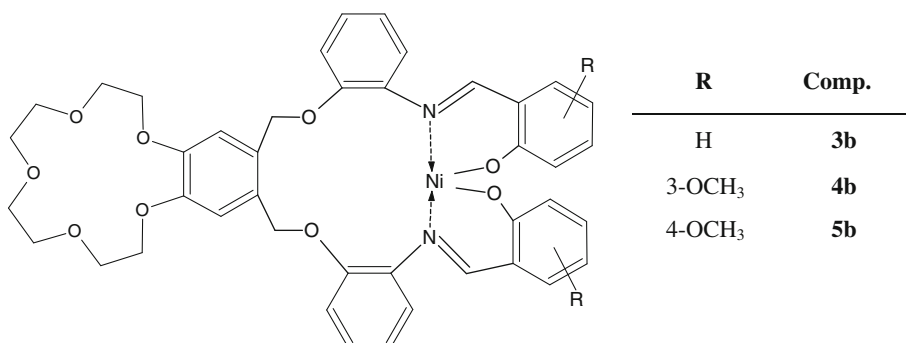


Scheme 1 Synthesis of new crown ethers

Scheme 2 Synthesis of new sodium complexes



Scheme 3 Synthesis of new nickel (II) complexes



sodium (**1a–5a**) and nickel(II) (**3b–5b**) complexes were obtained by direct reaction between ligands (**1–5**) and NaClO₄ and Ni(OAc)₂·4H₂O, respectively. All solid crown ether ligands and complexes were described and their IR,

¹H-, ¹³C-NMR, mass and UV–Vis spectral data were reported. The complexation ability of these crown ethers toward Li⁺, Na⁺, K⁺, Cr³⁺, Mn²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Pb²⁺, were measured by the solvent extraction method.

Experimental

Reagents and techniques

Tetraethylene glycol dichloride [12], benzo-15-crown-5 [1] and 4',5'-bis(bromomethyl)benzo-15-crown-5 [13] were prepared according to the literature. Salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) and 2-hydroxy-4-methoxybenzaldehyde were purchased from Aldrich and used without further purification. CH₃CN, THF, DMF and EtOH were dried by standard methods prior to use. Melting points were measured on a Thomas-Hoover apparatus using a capillary tube. ¹H- and ¹³C-NMR spectra were obtained on a Bruker DPX FT-NMR (400 MHz) spectrometer (SiMe₄, as an internal standard). Chemical shifts for proton and carbon resonances were reported in ppm (δ). IR spectra were obtained from a PEL-DATA spectrum 100 series spectrometer. UV–Vis spectra were recorded using a Unicam UV2-100 series spectrometer. Carbon, nitrogen and hydrogen analyses were performed on a LECO CHNS-932 elemental analyzer. Mass spectrometric analyses were performed on the AGILENT 1100 MSD spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MKI) at room temperature (25 °C).

Extraction studies

Alkali metal picrates were prepared according to the literature method [14]. Transition metal picrates were prepared by stepwise addition of a 1×10^{-2} M transition metal nitrate solution to a 1.17×10^{-4} M aqueous picric acid solution. The mixture was vigorously shaken at room temperature for 2 h. Equal volumes (10 mL) of a CHCl₃ solution of a crown ether (1×10^{-3} M) and of an aqueous alkali or transition metal picrate (1.17×10^{-4} M) were introduced into an erlenmeyer, which was then stoppered and vigorously shaken for 12 h at 25 °C with mechanical stirring. Measurements were taken after 2 h of shaking and subsequent 2 h of standing. After complete phase separation, the concentration of picrate ion in the aqueous phase was determined spectrophotometrically ($\lambda_{\text{max}} = 356$ nm). For each metal:crown ether system the absorbance measurements were repeated three times. Blank experiments showed that no picrate extraction occurred in the absence of the crown ether. The percentage of the extraction (E%) was determined based on the absorbance of picrate ion in the aqueous solutions. The extractability of alkali and transition metal picrates into the organic layer (CHCl₃) was calculated by the expression [15–19];

$$E\% = 100(A_0 - A)/A_0$$

where A_0 is the absorbance in the absence of crown ether and A denotes the absorbance in the aqueous phase after extraction.

Syntheses

15,16-bis[(2-nitrophenoxy)methyl]-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacycloptadecine (1)

The *o*-nitrophenol (0.15 g, 1.10 mmol) was dissolved in DMF (15 mL). NaOH (0.55 g, 1.36 mmol) was added in small amounts, and the resulting reaction mixture was refluxed for 1 h. Subsequently, 4',5'-bis(bromomethyl)benzo-15-crown-5 (0.25 g, 0.55 mmol) in DMF (15 mL) was added dropwise to the reaction mixture. The resulting solution was refluxed for 30 h, then the complete consumption of the starting material was observed by TLC (silica, eluent; THF). Then, water was added until the solution turned cloudy. The yellow precipitate formed was isolated and recrystallized from ethanol.

[2-({16-[(2-aminophenoxy)methyl]-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacycloptadecin-15-yl)methoxy}phenyl)amino-amin benzo-15-crown-5 (2)

The compound (1) (1.0 g, 1.70 mmol) was dissolved in EtOH (50 mL) by heating at 70 °C. The palladium/activated carbon (10%) (0.10 g) was added to the reaction flask at the same temperature and allowed to stand at 70 °C and then 12 mL hydrazine monohydrate (75%) was added dropwise within 1 h to the reaction mixture. The reaction mixture was refluxed and stirred for 4 h and then the mixture was filtered to remove charcoal. The white product was recrystallized from ethanol.

General methods for preparing Schiff bases (3–5)

The corresponding aldehydes (salicylaldehyde or 2-hydroxy-3-methoxybenzaldehyde or 2-hydroxy-4-methoxybenzaldehyde) (2.0 mmol) were dissolved in EtOH (20 mL). Double arm crown amine (1.0 mmol) was dissolved in EtOH and added dropwise. The resulting solution was stirred under reflux for 6 h and the reaction mixture was allowed to stand 2 h at room temperature. Yellow crystals formed and these were recrystallized from EtOH. Specific details for each compound are given in Table 1.

General methods for preparing sodium complexes (1a–5a)

The respective crown ether (1–5) (1.44 mmol) and NaClO₄ (0.17 g, 1.44 mmol) were dissolved in dry EtOH (10 mL)

Table 1 Analytical and experimental details

| Comp. | Formula | Color | Yield (%) | m.p. (°C) | Elemental analyses (%) found (calc) | | |
|-------|---|--------|-----------|----------------|-------------------------------------|-------------|-------------|
| | | | | | C | H | N |
| (1) | C ₂₈ H ₃₀ N ₂ O ₁₁ ·H ₂ O | Yellow | 38.62 | 156–160 | 57.32 (57.14) | 5.24 (5.48) | 4.93 (4.76) |
| (2) | C ₂₈ H ₃₄ N ₂ O ₇ | White | 75.83 | 140–144 | 65.72 (65.87) | 6.68 (6.71) | 5.52 (5.49) |
| (3) | C ₄₂ H ₄₂ N ₂ O ₉ | Yellow | 63.17 | 131–137 | 70.22 (70.18) | 5.91 (5.89) | 3.88 (3.90) |
| (4) | C ₄₄ H ₄₆ N ₂ O ₁₁ | Orange | 74.64 | 74–76 | 67.93 (67.85) | 5.95 (5.95) | 3.55 (3.60) |
| (5) | C ₄₄ H ₄₆ N ₂ O ₁₁ | Yellow | 72.92 | 143–149 | 67.85 (67.85) | 5.89 (5.95) | 3.61 (3.60) |
| (1a) | C ₂₈ H ₃₀ N ₂ O ₁₁ NaClO ₄ | White | 56.21 | 252–254 | 48.55 (48.53) | 4.37 (4.36) | 4.01 (4.04) |
| (2a) | C ₂₈ H ₃₄ N ₂ O ₇ NaClO ₄ | Brown | 93.54 | 213–215 | 53.26 (53.13) | 5.29 (5.41) | 4.55 (4.43) |
| (3a) | C ₄₂ H ₄₂ N ₂ O ₉ NaClO ₄ | Brown | 55.19 | – ^a | 60.32 (59.97) | 5.21 (5.03) | 3.12 (3.33) |
| (4a) | C ₄₄ H ₄₆ N ₂ O ₁₁ NaClO ₄ | Orange | 48.75 | 130–136 | 59.01 (58.64) | 5.22 (5.14) | 3.35 (3.11) |
| (5a) | C ₄₄ H ₄₆ N ₂ O ₁₁ NaClO ₄ | Yellow | 57.66 | 181–182 | 58.24 (58.64) | 5.02 (5.14) | 3.42 (3.11) |
| (3b) | NiC ₄₂ H ₄₀ N ₂ O ₉ ·1/2H ₂ O | Brown | 47.97 | 95–100 | 64.16 (64.31) | 5.23 (5.23) | 3.49 (3.57) |
| (4b) | NiC ₄₄ H ₄₄ N ₂ O ₁₁ ·5H ₂ O | Brown | 55.68 | 128–130 | 57.30 (57.10) | 5.26 (5.88) | 3.09 (3.03) |
| (5b) | NiC ₄₄ H ₄₄ N ₂ O ₁₁ ·1/2H ₂ O | Green | 27.67 | – ^a | 62.66 (62.35) | 5.45 (5.31) | 3.30 (3.30) |

^a The complexes are slowly decomposed >200 °C

and heated to reflux for 2 h. The precipitated complex was filtered and washed with diethyl ether. Specific details for each sodium complex are given in Table 1.

General methods for preparing nickel(II) complexes (3b–5b)

To a solution of respective crown ether (3–5) (1.16 mmol) in dry acetonitrile (50 mL) at room temperature was added a solution of Ni(OAc)₂·4H₂O (0.14 g, 1.17 mmol) in methanol (10 mL) with stirring. The mixture was refluxed for 4 h and the mixture was allowed to cool to room temperature. Then the mixture was filtered and dried in vacuum. Specific details for each nickel(II) complex are given in Table 1.

Results and discussion

Syntheses

The synthetic procedure for the preparation of the crown ether amine compound (2) consists of two steps. Firstly, *o*-nitrophenol was reacted with NaOH in DMF to give the corresponding sodium alkoxide and this sodium salt was converted to the corresponding new crown ether nitro compound (1) by reacting with 4',5'-bis(bromomethyl)benzo-15-crown-5. The compound (1) successfully synthesized with yield in the range of (38.62)%. Secondly, the aromatic primary amine (2) was prepared from compound (1) in EtOH using 10% palladium/activated charcoal and hydrazine monohydrate (75%) at 70 °C.

Direct reaction of one equivalent (2) with one equivalent appropriate aldehyde in ethanol gives the corresponding

crown ether Schiff bases (3–5). The sodium and nickel(II) complexes were prepared by treating a solution of the ligand in EtOH with NaClO₄ and Ni(OAc)₂·4H₂O, respectively. All the compounds are stable in solution. The structures of the ligands, alkali and transition metal complexes have verified by elemental analysis, FT-IR, ¹H-, ¹³C-NMR and mass spectra. Various attempts to obtain single crystals of the ligands and complexes have so far been unsuccessful.

Mass spectra and magnetic properties

The APCI and API-ES mass spectra of compounds were recorded. Compounds examined provided nice quality mass spectra and the molecular weight of the ligands and complexes have been confirmed. The mass spectrum of compound (1) which was obtained by the APCI technique shows an intensive signal at *m/z* 588.2 (100%). This signal assigned to [M + H₂O]⁺. The important fragments for compound (1) were detected at *m/z* 1158.3 (7.0%), 432.1 (42.3%), 325.1 (83.2%), 295.1 (18.4%) and 163.1 (14.8%) corresponding to the [2M + H₂O]⁺, [C₂₂H₂₆NO₈], [C₁₈H₁₈NO₅ – 3H], [C₁₆H₂₂NO₅ + H] and [C₇H₁₄O₄ + H] groups, respectively. API-ES mass spectrum and elemental analysis also confirm the formation of compound (2) at *m/z* 509.6 (100%) [M]⁺ and 1021.8 (28.2%) [2M + H]. The major fragments at *m/z* 400.2 (28.7%), 253.6 (7.8%) and 107.1 (10.3%) corresponding to the [C₂₂H₂₈NO₆ – 2H], [C₁₅H₁₄NO₃ – 3H] and [C₆H₆NO – H] groups, respectively. In the APCI mass spectra of Schiff bases (3 and 5) the respective molecular ion peaks [M + H] were detected at *m/z* 719.2 (6.8%) and 779.2 (51.2%). The major fragments of compound (3) were found at *m/z* 615.2 (71.9%), 402.2 (100%) and 214 (3.3%)

corresponding to the $[C_{38}H_{34}N_2O_6 + H]$, $[C_{24}H_{20}N_2O_4 + 2H]$ and $[C_{13}H_{10}NO_2 + 2H]$ groups, respectively. The important fragments of compound (**5**) were detected at 645.2 (100%), 536.2 (60.8%), 402.2 (95.9%) and 244.1 (26.0%) corresponding to the $[C_{38}H_{34}N_2O_8 - H]$, $[C_{30}H_{34}NO_8]$ $[C_{24}H_{20}N_2O_4 + 2H]$ and $[C_{14}H_{12}NO_3 + 2H]$ groups, respectively. In the API-ES mass spectrum of compound (**1a**) the dominant peak at m/z 591.8 (100%) corresponds to the ligand plus sodium $[M + Na]^+$. The important fragments of complex (**1a**) were observed at m/z 430.3 (37.9%) and 312.0 (11.8%) corresponding to the $[C_{22}H_{26}NO_8 - 2H]$ and $[C_{17}H_{16}NO_5 - 2H]$, respectively. In the API-ES mass spectra of the Ni(II) complex (**3b**), the molecular ion peak $[M + \frac{1}{2} H_2O]$ was observed at m/z 784.5 (3.7%). The important fragments were detected at m/z 407.2 (100%), 402.2 (77.8%) and 214.0 (56.9%) corresponding to the $[C_{25}H_{23}NO_4 + 6H]$, $[C_{25}H_{23}NO_4 + H]$ and $[C_{13}H_9NO_2 + 3H]$ groups, respectively. All of the mass spectra show that this fragmentation pattern proceeding by the loss of etheric chains is in accordance with literature [20]. The molecular ion peaks and fragments of the ligands and complexes support the proposed structures.

Magnetic susceptibility measurements provide sufficient data to characterize the nickel(II) complexes (**3b–5b**). The elemental analysis and the effective magnetic moments ($\mu_{\text{eff}} = 3.03, 3.02$ and 3.07 BM of the complexes **3b–5b**, respectively) confirm the presence of two unpaired electrons in a tetrahedral environment, in agreement with $e^4t_2^4$ configuration.

IR spectra

Selected IR data of the crown ethers alkali and transition metal complexes are shown in Table 2. In the IR spectra

both the characteristic internal $\nu(\text{NO}_2)$ and $\nu(\text{NH}_2)$ absorption bands are observed at 1510, 1343 cm^{-1} (N–O stretching) and 3386, 3363 cm^{-1} (N–H stretching), respectively. The Schiff bases (**3–5**) show strong bands at 1614, 1613 and 1612 cm^{-1} characteristic of the imine bond, attributable to the azomethine (HC=N) group. This stretching vibration confirms the presence of imine group and the absence of aromatic primary amine group of the starting materials. The spectra of all compounds (**1–5**) are dominated by bands between 2972 and 2850 cm^{-1} due to $\nu(\text{C–H})_{\text{aliph}}$ groups.

The spectra of the sodium complexes (**1a–5a**) are approximately the same as the Schiff base spectra. All the perchlorate complexes featured split bands attributable to the asymmetric, $\nu_{\text{asym}}(\text{Cl–O})$, stretching mode at ca. 1050–1092 cm^{-1} and the asymmetric, $\nu_{\text{asym}}(\text{O–Cl–O})$, bending mode at 620–626 cm^{-1} , as befits an uncoordinated anion [21].

The IR spectra of the complexes (**3b–5b**), the shift of $\nu(\text{C=N})$ from 1614, 1613 and 1612 cm^{-1} in the Schiff bases to very strong absorption bands in the region 1608, 1607 and 1608 cm^{-1} in the nickel(II) complexes, suggests the formation of a C=N–M band system. The shift to lower frequency by about 6 cm^{-1} in the nickel(II) complexes indicates the coordination of oxygen to metal ions.

^1H - and ^{13}C -NMR spectroscopy

In order to identify structure of the nitro (**1**) and amine (**2**) substituted benzo15-crown-5, Schiff bases (**3–5**), alkali metal complexes (**1a**, **2a** and **4a**) ^1H -NMR spectra were recorded in CDCl_3 , acetone and DMSO. The chemical shifts, expressed in ppm downfield from tetramethylsilane, are given in Table 3.

Table 2 Selected IR bands

| Comp. | $\nu(\text{C=C})$ | $\nu(\text{C–H})_{\text{aliph}}$ | $\nu(\text{NO}_2)$ | $\nu(\text{NH}_2)$ | $\nu(\text{C=N})$ | $\nu(\text{C–O–C})_{\text{arom}}$ | $\nu(\text{C–O–C})_{\text{aliph}}$ | $\nu(\text{ClO}_4^-)$ |
|-----------|-------------------|----------------------------------|--------------------|--------------------|-------------------|-----------------------------------|------------------------------------|-----------------------|
| 1 | 1581 (m) | 2952; 2860 (m) | 1510; 1343 (s) | – | – | 1325; 1256 (m) | 1136; 1071 (m) | – |
| 2 | 1504; 1456 (m) | 2972; 2876 (m) | – | 3386; 3363 (m) | – | 1323; 1299 (m) | 1117; 1060 (s) | – |
| 3 | 1514; 1451 (w) | 2918; 2850 (m) | – | – | 1614 (m) | 1342; 1281 (m) | 1118; 1084 (s) | – |
| 4 | 1516; 1460 (m) | 2929; 2868 (m) | – | – | 1613 (s) | 1366; 1276 (s) | 1113; 1079 (s) | – |
| 5 | 1513; 1449 (m) | 2918; 2850 (m) | – | – | 1612 (s) | 1338; 1288 (m) | 1135; 1030 (m) | – |
| 1a | 1583 (m) | 2928; 2879 (w) | 1516; 1340 (s) | – | – | 1275 (s) | 1100; 1081 (s) | 1050 (s); 623 (m) |
| 2a | 1516; 1454 (m) | 2923; 2878 (w) | – | 3382; 3366 (m) | – | 1334; 1276 (s) | 1115; 1062 (s) | 1082 (s); 623 (m) |
| 3a | 1512; 1490 (m) | 2971; 2902 (m) | – | – | 1615 (m) | 1364; 1281 (m) | 1100; 1063 (s) | 1084 (s); 620 (m) |
| 4a | 1515; 1461 (m) | 2937; 2879 (w) | – | – | 1614 (m) | 1366; 1250 (s) | 1113; 1058 (s) | 1092 (s); 624 (m) |
| 5a | 1513; 1493 (s) | 2971; 2901 (m) | – | – | 1615 (s) | 1357; 1240 (m) | 1106; 1029 (s) | 1070 (s); 626 (m) |
| 3b | 1519; 1490 (s) | 2971; 2901 (m) | – | – | 1608 (s) | 1341; 1250 (m) | 1107; 1056 (s) | – |
| 4b | 1517; 1439 (m) | 2930; 2867 (w) | – | – | 1611 (m) | 1387; 1285 (m) | 1117; 1079 (s) | – |
| 5b | 1514; 1494 (s) | 2967; 2878 (w) | – | – | 1608 (s) | 1321; 1241(m) | 1117; 1050 (s) | – |

w weak, m medium, s strong

Table 3 Selected $^1\text{H-NMR}$ spectral data

| Comp. | NH_2 | $\text{OCH}_2\text{CH}_2\text{O}$ | $-\text{OCH}_3$ | Ar-H | $-\text{CH}_2$ | N=CH | OH |
|-----------------------|---------------|-----------------------------------|-----------------|-------------------|----------------|--------------|---------------|
| 1^a | – | 3.76–4.25 (m, 8H) | – | 7.05–7.86 (m, 5H) | 5.35 (s, 2H) | – | – |
| 2^b | 4.28 (s, 2H) | 3.55–4.25 (m, 8H) | – | 6.41–7.06 (m, 5H) | 5.05 (s, 2H) | – | – |
| 3^a | – | 3.79–4.18 (m, 8H) | ^d | 6.92–7.47 (m, 9H) | 5.20 (s, 2H) | 8.52 (s, 1H) | 13.80 (s, 1H) |
| 4^a | – | 3.77–4.10 (m, 8H) | ^d | 6.85–7.40 (m, 8H) | 5.23 (s, 2H) | 8.62 (s, 1H) | 14.30 (s, 1H) |
| 5^a | – | 3.78–4.15 (m, 8H) | ^d | 6.45–7.20 (m, 8H) | 5.20 (s, 2H) | 8.53 (s, 1H) | 14.45 (s, 1H) |
| 1a^a | – | 3.38–4.32 (m, 8H) | ^d | 7.03–9.00 (m, 5H) | 5.30 (s, 2H) | – | – |
| 2a^a | 4.29 (s, 2H) | 3.72–4.30 (m, 8H) | ^d | 7.10–7.88 (m, 5H) | 5.35 (s, 2H) | – | – |
| 3a | – | 3.73–4.18 (m, 8H) | – | 6.91–7.35 (m, 9H) | 5.14 (s, 2H) | 8.68 (s, 1H) | 13.88 (s, 1H) |
| 4a^c | – | 3.74–4.30 (m, 8H) | ^d | 6.82–7.24 (m, 8H) | 5.15 (s, 2H) | 8.65 (s, 1H) | 14.39 (s, 1H) |

Chemical shifts (δ), in ppm (s: singlet, m: multiplet)

^a CDCl_3 , ^b Acetone, ^c DMSO, ^d Overlapping with $\text{OCH}_2\text{CH}_2\text{O}$ peaks

The dinitro (**1**) and diamine (**2**) spectra indicate that the molecules are symmetric; therefore, five different aromatic protons (H_{1-5}) were detected at δ 7.05–7.86 and 6.41–7.06 ppm, respectively. The peaks of the crown ether protons ($-\text{OCH}_2-\text{CH}_2\text{O}-$) for compounds (**1** and **2**) were seen to resonate between at δ 3.76–4.25 and 3.55–4.25 ppm, respectively. The $-\text{CH}_2$ protons were observed as a singlet at 5.35 and 5.05 ppm for the compounds (**1** and **2**). The N–H band was detected at δ 4.28 ppm as a broad singlet. The Schiff bases (**3–5**) spectra indicate that the molecules were symmetric as compound **1** and **2**. The absence of primary aromatic amine groups belonging to compound (**2**) has also supported the formation of Schiff bases (**3–5**). The imine peaks for compounds (**3–5**) were observed as singlet at δ 8.52, 8.62 and 8.53 ppm, respectively. The observation of these singlets provides confirmation of Schiff base reaction between crown ether amine with appropriate aldehyde. The methoxy ($-\text{OCH}_3$) protons were detected for compound (**3–5**) as a singlet in crown ether protons region. Although the structures of the imine compounds (**3–5**) were symmetric, however the assignments of the aromatic protons were highly complicated in the region 6.92–7.47, 6.85–7.40 and 6.45–7.20 ppm, respectively. The chemical shifts have been determined by comparison with nitro (**1**) and amine (**2**) compounds which have shown protons of the $-\text{OCH}_2-\text{CH}_2\text{O}-$ and $-\text{CH}_2$ to be located as expected. The $^1\text{H-NMR}$ spectra of the sodium complexes (**1a**, **2a** and **4a**) were approximately the same as in the corresponding ligand spectra. It is well known [22–24] that the Na^+ cations, on the other hand are sufficiently small to fit into the cavities of benzo-15-crown-5 moieties of the crown ethers (**1–5**). According to the literature [22], the complexation of the ligands (**1–5**) with Na^+ cations can be call “filling complexes”. In conventional “filling complexes”, low chemical shifts are especially observed for the aromatic and crown ether protons. The four-coordinate functionalized complexes (**3b–5b**) were prepared by the condensation of Schiff

bases N_2O_2 donor atoms. The above mentioned facts showed that Schiff base ligand (**3–5**) can coordinate with nickel(II) ion as in Scheme 3. The nickel(II) complexes (**3b–5b**), the nickel(II):ligand mole ratio were found to be 1:1 according to elemental analysis. Since all of the Ni(II) complexes (**3b–5b**) are paramagnetic, because of their NMR spectra could not be detected.

The $^{13}\text{C-NMR}$ spectral data and numbering of the carbons for $^{13}\text{C-NMR}$ were given in Table 4. The signals of the eight crown ether carbons are observed between at 68.59–71.59 ppm. The signals for the $-\text{OCH}_3$, $-\text{CH}_2$ and aromatic ring carbons were detected in the corresponding region.

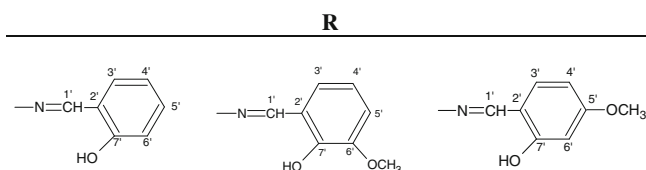
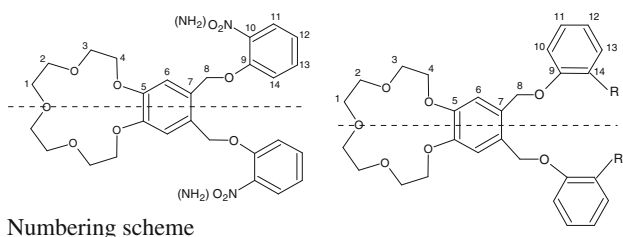
Extraction studies using UV/Vis spectrophotometer

Extraction is a simple and useful method for evaluating the complexing ability of crown ethers with alkali and transition metal cations. The results, expressed as a percentage of cation extracted (%E), are collected in Table 5 and show graphically in Fig. 1. The alkali metal cations (Li^+ , Na^+ and K^+) and transition metal cations (Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Cr^{3+} , Mn^{2+}) complexing abilities of the crown ethers (**1**, **3–5**) were assessed by solvent extraction of aqueous alkali and transition metal picrates with chloroform solution of the above compounds. The data in Table 5 indicates that compound **1** shows the highest extractability towards K^+ , compounds **3** and **4** towards Cr^{3+} and compound **5** towards Cu^{2+} when compared with other cations. The levels of extraction for Mn^{2+} and Zn^{2+} are low extractability for all of the compounds (**1**, **3–5**). The extraction trend observed for Schiff bases (**3–5**) are nearly same extraction profile. As can be seen from Table 5, compound (**1**) has higher selectivity for K^+ (49.4%). Compounds (**3–5**) are also poor extractant showing for K^+ (8.9, 7.6 and 4.8%, respectively) however, some preference for Cr^{3+} , Cu^{2+} and Pb^{2+} when compared to compound **1**.

Table 4 Selected ^{13}C -NMR spectral data (δ , ppm)

| Comp. | C _{1–4} | C ₅ | C ₆ | C ₇ | C ₈ | C _{9–14} | C _{1=N} | C _{2'–7'} | –OCH ₃ |
|----------------------|-------------------------------|----------------|----------------|----------------|----------------|---|------------------|---|-------------------|
| 1^a | 69.07; 69.76; 70.79; 71.46 | 149.23 | 115.40 | 127.47 | 69.48 | 115.90; 121.22; 125.72; 134.88; 140.58; 151.89 | – | – | – |
| 2^b | 69.21; 69.56; 70.54; 71.13 | 148.95 | 112.59 | 128.54 | 68.25 | 115.24; 115.54; 118.39; 121.76; 136.72; 145.30 | – | – | – |
| 3^b | 69.40; 70.07; 70.99; 71.59 | 152.55 | 114.70 | 128.66 | 68.72 | 114.88; 120.49; 122.25; 128.21; 138.63; 149.50 | 163.43 | 117.98; 119.53; 120.16; 132.86; 133.77; 162.50 | – |
| 4^b | 68.59; 69.58; 70.59; 71.15 | 152.55 | 114.14 | 128.34 | 67.92 | 114.57; 119.27; 121.48; 127.28; 137.34; 148.61 | 162.49 | 118.17; 119.27; 119.87; 127.28; 151.51; 152.23 | 56.07 |
| 5^b | 69.41; 70.10; 70.97; 71.58 | 152.27 | 113.94 | 128.19 | 68.72 | 114.72; 115.78; 120.11; 122.25; 138.06; 148.47 | 166.38 | 101.82; 107.61, 114.90; 134.18; 161.78; 165.10 | 55.74 |

^a d⁶-DMSO + CDCl₃, ^b CDCl₃

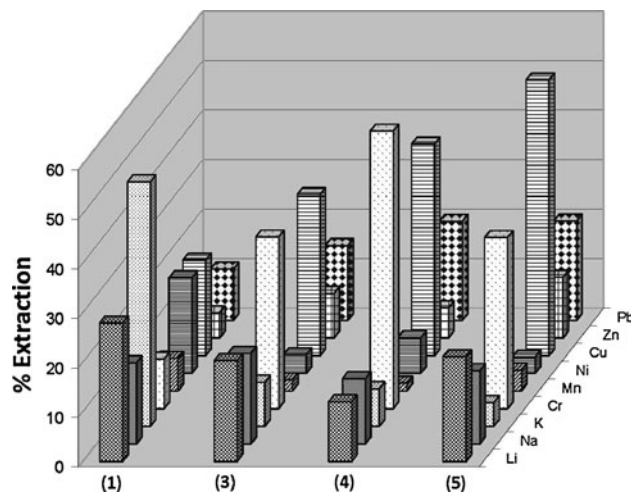
**Table 5** Alkali and transition metal picrate extractions for compounds (1, 3–5) into chloroform phase

| Metal ion | Extractability (%) ^a | | | |
|------------------|---------------------------------|------------|------------|------------|
| | (1) | (3) | (4) | (5) |
| Li ⁺ | 28.0 ± 0.3 | 20.4 ± 05 | 12.1 ± 0.2 | 21.2 ± 0.1 |
| Na ⁺ | 16.4 ± 0.2 | 18.3 ± 0.4 | 13.2 ± 0.5 | 14.8 ± 0.2 |
| K ⁺ | 49.4 ± 0.5 | 8.9 ± 0.7 | 7.6 ± 0.3 | 4.8 ± 0.2 |
| Cr ³⁺ | 10.0 ± 0.7 | 34.7 ± 0.4 | 56.1 ± 0.1 | 34.6 ± 0.4 |
| Mn ²⁺ | 6.6 ± 0.4 | 2.3 ± 0.1 | 1.6 ± 0.6 | 4.2 ± 0.6 |
| Ni ²⁺ | 19.3 ± 0.1 | 3.8 ± 0.8 | 7.2 ± 0.1 | 3.3 ± 0.3 |
| Cu ²⁺ | 19.3 ± 0.5 | 32.6 ± 0.5 | 42.8 ± 0.7 | 55.7 ± 0.2 |
| Zn ²⁺ | 5.1 ± 0.7 | 9.0 ± 0.2 | 6.1 ± 0.5 | 12.3 ± 0.7 |
| Pb ²⁺ | 10.4 ± 0.5 | 15.1 ± 0.7 | 20.0 ± 0.2 | 20.1 ± 0.2 |

Temperature 25 ± 1 °C; aqueous phase (10 mL); [pic[−]] = 1.17 × 10^{−4} M, organic phase (10 mL chloroform); [L] = 1 × 10^{−3} M. [M⁺] picrate; 1.17 × 10^{−4} M.

^a Average for three samples

From the extraction data shown in Table 5, it can be seen that the ligands (1, 3–5) show moderately affinity for Li⁺ and Na⁺ ions (%E ranges from 12.1 to 28.0). Na⁺ is similarly extracted for all compounds (1, 3–5). It is interesting that the percentage of the extraction of K⁺ ion with compound (1) is higher than that of Li⁺ and Na⁺ ions extractability. Schiff bases (3–5) exhibits extraction percentages higher than for compound 1 for Cr³⁺, Cu²⁺ and

**Fig. 1** Percentages extraction (%E) of different metal picrates [M⁺] picrate; 1.17 × 10^{−4} M into chloroform at 25 ± 1 °C

Pb²⁺ studied. From the results it is apparent that the compounds (3–5) are poor extractants for the K⁺, Mn²⁺, Ni²⁺ and Zn²⁺. It is clear that the extractability results of the ligands are different. Our results suggest that the match between the alkali and transition metal cation and benzo-15-crown-5 cavity dimensions is not seem to be an important factor in cation selectivity. The complexation ability of the ligand with various alkali and transition metal

ions may depend on flexibility of macrocyclic ring, substituent which cause changing the conformation and flexibility [25]. On the other hand, the hard and soft acids and bases principle is seem to be an important factor in selectivity for some compounds [26]. Because, our compounds (3–5) contain hard oxygen donor atoms, they show preference for Cr^{3+} (especially compound 4). Consequently, no simple explanation for the observed extraction selectivity is apparent from these results, and other factors involving the hosts and guests must be considered. Different substituent and side arms of the crown ether rings lead to different arrangements of the donor atoms in the crown ethers, and also the metal cation have different geometrical requirements and different extraction ranges.

The liquid–liquid extraction processes involving alkali and transition metal picrates are usually characterized as equilibria that are described by the following equation:



where the subscript (aq) and (org) stand for aqueous and organic phases (CHCl_3), respectively. The overall extraction equilibrium constant (K_{ex}) can be written as:

$$K_{\text{ex}} = \frac{[\text{M}(\text{L})_m(\text{Pic})_n]_{\text{org}}}{[\text{M}^{n+}]_{\text{aq}} [\text{Pic}^-]_{\text{aq}}^n [\text{L}]_{\text{org}}^m}$$

The resulting calculated for compounds (1, 3–5) extraction equilibrium constant $\log(K_{\text{ex}})$ values are presented in Table 6. The extraction constants for Cr^{3+} ion are higher than other metal ions for all compounds (1, 3–5) and the extraction constants were calculated as 15.91, 16.47, 17.16 and 16.46, respectively. These results show that the hard metal ion is very effective on extraction efficiency. Consequently, the high extraction constant values may result from the stability of the mentioned complexes.

The distribution ratios for each cation, D , defined as the ratio between the extracted amount of alkali and transition metal picrate (in organic phase) and the remaining metal

Table 6 The extraction constants for compounds (1, 3–5)

| Comp. | Extraction equilibrium constant ($\log K_{\text{ex}}$) ^a | | | | | | | | |
|-------|---|---------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | Li^+ | Na^+ | K^+ | Cr^{3+} | Mn^{2+} | Ni^{2+} | Cu^{2+} | Zn^{2+} | Pb^{2+} |
| (1) | 8.15 | 8.02 | 12.69 | 15.91 | 11.88 | 12.07 | 12.07 | 11.86 | 11.94 |
| (3) | 8.06 | 8.04 | 12.93 | 16.47 | 11.83 | 11.85 | 12.31 | 11.92 | 12.01 |
| (4) | 7.98 | 7.99 | 12.98 | 17.16 | 11.82 | 11.89 | 12.52 | 11.88 | 12.09 |
| (5) | 8.07 | 8.00 | 13.26 | 16.46 | 11.85 | 11.84 | 12.86 | 11.97 | 12.09 |

^a Extraction equilibrium constants were calculated taking into consideration of benzo-15-crown-5 cavity and metal ion diameter (complex compositions (L:M) are 1:1 for Li^+ , Na^+ , Cr^{3+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Pb^{2+} , only K^+ complex composition is 2:1) [27, 28]

Table 7 The distribution constants for compounds (1, 3–5)

| Comp. | Distribution constant (D) | | | | | | | | |
|-------|---------------------------|---------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | Li^+ | Na^+ | K^+ | Cr^{3+} | Mn^{2+} | Ni^{2+} | Cu^{2+} | Zn^{2+} | Pb^{2+} |
| (1) | 0.39 | 0.20 | 0.98 | 0.11 | 0.07 | 0.24 | 0.24 | 0.05 | 0.12 |
| (3) | 0.26 | 0.22 | 0.10 | 0.53 | 0.02 | 0.04 | 0.48 | 0.10 | 0.18 |
| (4) | 0.14 | 0.15 | 0.08 | 1.28 | 0.02 | 0.08 | 0.75 | 0.06 | 0.25 |
| (5) | 0.27 | 0.17 | 0.05 | 0.53 | 0.04 | 0.03 | 1.26 | 0.14 | 0.25 |

picrate in aqueous phase, were computed using the expression:

$$D = \frac{[\text{M}(\text{L})_m(\text{Pic})_n]_{\text{org}}}{[\text{M}^{n+}]_{\text{aq}}}$$

It follows that

$$D = K_{\text{ex}} [\text{Pic}^-]_{\text{aq}}^n [\text{L}]_{\text{org}}^m$$

The distribution ratios determined for each compound (1, 3–5) towards each alkali and transition metal cations are presented in Table 7.

Conclusion

In summary, we have prepared new crown ether nitro (1), amine (2) and Schiff base compounds (3–5). Mononuclear sodium perchlorate (1a–5a) and nickel(II) complexes (3b–5b) of the new host compounds have been synthesized and characterized. Magnetic moments and spectroscopic data show that nickel(II) complexes complete the coordination number four by tetradentate (N_2O_2 type) ligand. Consequently, the nickel(II) atoms are coordinated by two phenolic-O atoms and two azomethine-N atoms to form a tetrahedral geometry. The ligand complexing properties were studied by solvent extraction of selected alkali and transition metals (Li^+ , Na^+ , K^+ , Cr^{3+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Pb^{2+}). Extraction studies with Cr^{3+} and Cu^{2+} picrates from aqueous solution into chloroform have shown that Schiff bases (3–5) are better phase transfer agents and also more selective than nitro compound (1).

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References

- Pedersen, C.J.: Cyclic polyethers and their complexes with metal salts. *J. Am. Chem. Soc.* **89**, 7017–7036 (1967)
- Dixon, S., Brown, R.C.D., Gale, P.A.: A biaryl cross-coupling strategy for functionalisation of benzocrown ethers. *Chem. Commun.* 3565–3567 (2007)

- Chan, S.H., Wong, W.T., Chan, W.K.: Synthesis and properties of polyimide with diazacrown ether moiety and the corresponding polymer Barium complexes. *Chem. Mater.* **13**, 4635–4641 (2001)
- Coco, S., Cordovilla, C., Espinet, P., Gallani, J.-L., Guillon, D., Donnio, B.: Supramolecular aggregates in fluid phases: mesomorphic *ortho*-palladated complexes with substituted crown ethers and their potassium adducts. *Eur. J. Inorg. Chem.* 1210–1218 (2008)
- Beer, P.D., C.G., Crane, Drew, M.G.M.: Synthesis and co-ordination chemistry of new Schiff-base bis(crown ether) ligands containing recognition sites for alkali- and transition-metal guest cations. Crystal structure of a copper(I)–potassium complex. *J. Chem. Soc. Dalton Trans* 3235–3242 (1991)
- Hayvali, Z., Gunduz, N., Kilic, Z., Weber, E.: Synthesis, complex formation and spectral investigation of new tritopic bis(crown ether) compounds containing recognition sites for sodium and nickel guest cations. *Z.Naturforsch* **55b**, 975–981 (2000)
- Hayvali, Z., Gunduz, N., Kilic, Z., Weber, E.: Synthesis and characterization of new bis(crown ether)s of Schiff base type containing recognition sites for sodium and nickel guest cations. *J. Prakt. Chem* **341**(6), 568–573 (1999)
- Hayvali, Z., Hayvali, M., Kilic, Z., Hokelek, T., Weber, E.: New benzo-15-crown-5 ethers featuring salicylic Schiff base substitutions synthesis, complexes and structural study. *J. Incl. Phenom. Macrocycl. Chem.* **45**, 285–294 (2003)
- Hayvali, Z., Yardımcı, D.: Synthesis and spectroscopic characterization of asymmetric Schiff bases derived from 4'-formylbenzo-15-crown-5 containing recognition sites for alkali and transition metal guest cations. *Transition. Met. Chem.* **33**, 421–429 (2008)
- Berry, N.G., Shimell, T.W., Beer, P.D.: Heteroditopic transition metal dithiocarbamate receptors for binding cation-anion ion pairs. *J. of Supramolecular Chem* **2**, 89–92 (2002)
- Li, J., Xu, B., Jiang, W., Zhou, B., Zeng, W., Qin, S.: Catalytic epoxidation performance and dioxygen affinities of unsymmetrical Schiff base transition–metal complexes with pendant azacrown or morpholino groups. *Transition. Met. Chem.* **33**, 975–979 (2008)
- Calverly, M.J., Dale, J.: 1,4,7-Trioxa-10-azacyclododecane and some *N*-substituted derivatives: synthesis and cation complexing. *Acta Chem. Scand.* **36B**, 241–247 (1982)
- Winkler, B., Mau, A.W.-H., Dai, L.: Crown ether substituted phenylenevinylene oligomers: Synthesis and electroluminescent properties. *Phys. Chem. Chem. Phys.* **2**, 291–295 (2000)
- Bilgin, A., Ertem, B., Dinc Agin P., Gok Y., Karshloglu S.: Synthesis, characterization and extraction studies of new *vic*-dioxime and its complexes containing bis(diazacrown ether) moieties. *Polyhedron* **25**, 3165–3172 (2006)
- Ocak, U., Alp, H., Gokce, P., Ocak, M.: The synthesis of new N₂S₂-macrocyclic Schiff base ligands and investigation of their ion extraction capability from aqueous media. *Separation Science and Tech* **41**, 391–401 (2006)
- Kantekin, H., Ocak, U., Gok, Y., Acar, I.: The synthesis and characterization of a novel *vic*-dioxime and its mononuclear complexes bearing an 18-membered ₂O₂S₂ macro-cycle and their characteristics as extractants for transition metal ions. *J. Incl. Phenom. Macrocycl. Chem.* **48**, 95–101 (2004)
- Ocak, M., Alp, H., Kantekin, H., Karadeniz, H., Ocak, U.: Ion-pair extraction of transition metal cations from aqueous media using novel N₂O₂-macrocyclic crown ligands. *J. Incl. Phenom. Macrocycl. Chem.* **60**, 17–24 (2008)
- Seyedi, S.M., Shadkam, M., Ziafati, A.: A convenient synthesis of new macrocyclic thioether-esters and ether-esters: extraction properties of these esters for alkali, alkaline Earth, and transition metal cations. *Phosphorus, Sulfur, and Silicon* **180**, 1953–1960 (2005)
- Dede, B., Ozmen, I., Karipcin, F.: Synthesis, characterization, catalase functions and DNA cleavage studies of new homo and heteronuclear Schiff base copper(II) complexes. *Polyhedron* **28**, 3967–3974 (2009)
- Hayvali, Z., Hayvali, M., Dal, H.: Synthesis and spectroscopic characterization of new Schiff bases containing the benzo-15-crown-5 moiety. *Molecules* **9**, 860–866 (2004)
- Vicente, M., Lodeiro, C., Adams, H., Bastida, R., Blas, A., Fenton, D.E., Macias, A., Rodriguez, A., Rodriguez-Blas, T.: Synthesis and characterization of some metal complexes with new nitrogen–oxygen donor macrocyclic ligands—x-ray crystal structures of a 26-membered reduced monoprotonated macrocycle and a 20-membered pendant-arm Schiff-base macrocyclic cadmium(II) complex. *Eur. J. Inorg. Chem.* 1015–1024 (2000)
- Kleinpeter, E., Starke, I., Ströhl, D., Holdt, H.J.: NMR spectroscopic study of solution structure and complexational behaviour of bis-benzo crown ethers. *J. Mol. Struct.* **404**, 273–290 (1997)
- Beer, P.D.: The synthesis of a novel Schiff base bis(crown ether) ligand containing recognition sites for alkali and transition metal guest cations. *J. Chem. Soc. Commun* 1678–1680 (1986)
- Santhana Mariappan, S.V., Gomathi, L., Subramanian, S.: Structural changes in the complexation of benzo-crown ethers—NOESY and variable-temperature ¹³C NMR study. *Magn. Res. Chem* **29**, 656–666 (1991)
- Weber, E., Skobridis, K., Ouchi, M., Hakushi, T., Inoue, Y.: Polytopic cation receptors. III. Di- and tri-loop crown hosts having aromatic junctions. Synthesis, cation extraction, and solid complex formation. *Bull. Chem. Soc. Jpn.* **63**, 3670–3677 (1990)
- Marcos, P.M., Ascenso, J.R., Segurado, M.A.P., Pereira, J.L.C.: *p*-Tert-butylldihomooxalix[4]arene/*p*-tert-butylcalix[4]arene: Transition and heavy metal cation extraction and transport Studies by ketone and ester derivatives. *J. Incl. Phenom. Macrocycl. Chem.* **42**, 281–288 (2002)
- Takeda, Y., Wada, Y., Fujiwara, S.: The solvent extraction of alkali metal picrates by benzo-15-crown-5. *Bull. Chem. Soc. Jpn.* **54**, 3727–3730 (1981)
- Mouveaux, C., Levalois-Mitjaville, J., De Jaeger, R.: Complexation studies of phosphorus containing bis and tris (benzocrown ether) moieties. *J. I Incl. Phenom. Macrocycl. Chem.* **39**, 253–259 (2001)