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ORIGINAL PAPER

Selective removal of hard metal ions from water using benzo-crown ether derivatives: A lewis acid–base interaction approach

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Abstract

The hydrophilic internal cavities of crown ethers are enable complexation with metal ions, while their apolar exterior allows operation in organic solvents. In this study, benzo-thio-oxa crown ether derivatives (C1 and C2), synthesized via microwave-assisted methods, were evaluated for the extraction of metal ions from tap and stream water samples collected from Siirt and Şırnak provinces using liquid–liquid ion-pair extraction. The ligands showed preferential extraction toward selected metal ions depending on their donor atom composition and macrocyclic structure. For this purpose, benzothia crown ether compounds (C1 and C2) obtained by the microwave-assisted synthesis method were tested on tap and stream water samples (Samples I-III) taken from Siirt and Şırnak provinces by the liquid–liquid ion pair extraction method. While compound C1 (bis(1,2-dibenzo)octathio tetracarbonyl-36-crown-8) has fewer ether bridges and one thioether group, compound C2 (bis(1,2-dibenzo)tetrathio tetracarbonyl-42-crown-10) shows selectivity towards different ions, as it contains more ether bridges and one ester group. While C1 removes especially iron (total Fe) with high efficiency, compound C2 exhibited higher extraction efficiency against metal ions such as Zn^{2+}, Ca^{2+}, Sb^{3+}, Mg^{2+}, Mn^{2+}, and Ni^{2+}. Furthermore, partial decreases in anions such as F^{-}, PO_4^{3-}, SO_4^{2-}, and NO_3^{-} were observed following metal ion extraction, indicating concurrent changes in the ionic composition of the water samples. Post-treatment conductivity measurements indicated a 3–13% decrease in total dissolved ionic content. These findings underline the structure–function relationship of benzo-crown ether derivatives and indicate their potential use as tunable systems for selective metal ion removal, with possible future integration into water treatment materials.

Keywords Benzo thio crown ether · Metal complexation · Liquid-liquid ion pair extraction · Metal removal from water

Introduction

Access to safe drinking water is a fundamental requirement for human health. Prioritising the enhancement of water quality for safe consumption is essential because only around 1% of the planet's water is drinkable. Numerous pollutants are released by human activity, and the fact that these pollutants' concentrations vary by nation suggests that the current approaches may soon be insufficient. This situation necessitates the implementation of new measures to address emerging contaminants (Polat 2009). Organisms can be harmed by ions at both low and high concentrations. Whether from overexposure or deficiency, excessive levels of ions and heavy metals can cause health issues. For example, too much copper can lead to nausea, liver, and kidney damage, while too little copper can cause anaemia and problems with the nervous system (Edzwald 2011). In a similar vein, drinking tap water tainted with arsenic can cause vomiting, diarrhoea, and abdominal pain (WHO 2011). Lead contamination, which affects the nervous system directly, can cause serious kidney and brain damage or even death (US EPA 2025). Several methods are used to remove ions from water samples. These methods include evaporation, crystallization, solvent extraction, adsorption, precipitation, ion exchange, osmosis, electrolysis, and electrodialysis, among others (Ince and Kaplan Ince 2020; Selvaraj et al. 2020). Removal of Fe^{3+} ions from wastewater with 91.83% efficiency using an an environmentally friendly ultrasonic

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method was successfully achieved using CBZ-alcohol (Gökmen Karakaya et al. 2025). Traditional precipitation techniques are not very effective at removing heavy metals from industrial wastewater, despite the possibility of laboratory studies (Fabiani 1992). An alternative that is more effective, selective, and scalable is ion exchange (Benalla 2022). Particularly with new-generation organic and inorganic ion exchangers, the application area and efficacy are growing dramatically (Hubicki and Jusiak 1978; Hubicki and Pawlowski 1986; Hubicki et al. 1999). Adsorption is a common method for removing heavy metals from water and wastewater because of its high efficiency and ease of use. Adsorption is a cost-effective method for treating wastewater by retaining heavy metals, which depends on operating conditions and the properties of the materials used (Yang et al. 2019; Chowdhury et al. 2022). Although nanoparticles and carbon nanotubes are effective adsorbents due to their large surface areas, their high cost and difficulty in regenerating limit their application. Therefore, activated carbon-based functional adsorbents, obtained with environmentally friendly methods, emerge as a sustainable and preferred alternative because of their low cost and high performance (Marciniak et al. 2019; Owalude and Tella 2016). Adsorption was employed as a removal method using various types of modified bentonite, and their ability to effectively eliminate heavy metals from wastewater was examined. Most of the modified bentonite demonstrated good potential for heavy metal adsorption (Prabhu and Prabhu 2018).

Crown ethers and particular cations form complexes that are extremely stable and can be separated as crystals.

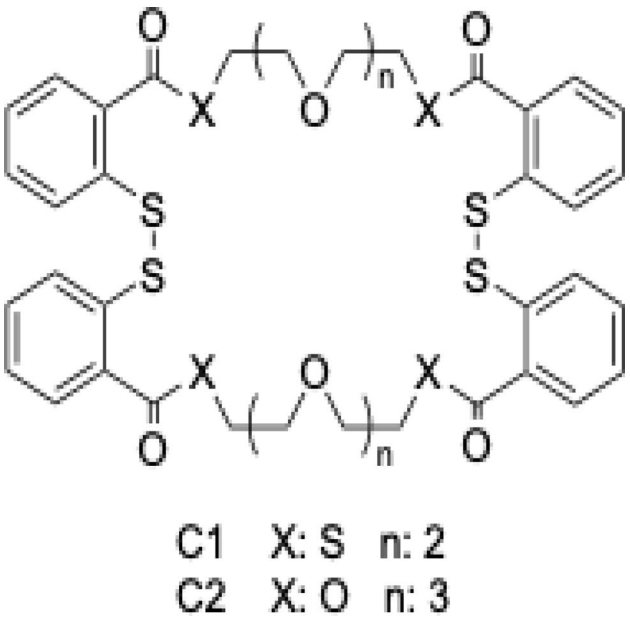

Fig. 1 Molecular structures of C1 (bis(1,2-dibenzo)octathio tetracarbonyl-36-crown-8) and C2 (bis(1,2-dibenzo)tetrathio tetracarbonyl-42-crown-10) used in this study

Pedersen first synthesised these complexes in the 1960s. Because of their interaction with metal ions, these cyclic complexes are used extensively (Parker 2002). Crown ethers can be classified into various types, including oxo, azo, thio, benzo, and benzothio, depending on the oxygen, sulfur, and nitrogen atoms they contain, as well as the presence of benzene rings. The synthesis of compounds containing sulphur started in the 1970s and 1980s, following Pedersen's synthesis of benzo crown ethers in the 1960s (Pedersen 1967). The synthesis of benzothiocyanate crown ethers, initiated by Tanaka and colleagues in 1972–1973 (Tanaka et al. 1972, 1973) and continued by Buter and Kellogg in 1981 (Buter and Kellogg 1981), saw significant expansion in the 1990s. This increase is consistent with the unique characteristics of sulfur donor atoms and benzene rings, as well as their propensity to bind to various metal ions. Compounds containing these groups are of great importance (Cicek et al. 2012). Thiocyanate crown ethers are particularly valuable for heavy and precious metal ions due to the sulfur atoms they contain (Yordanov and Roundhill 1998; Bruening et al. 1991; Nabeshima et al. 1969; Lindoy and Bush 1969). Heavy metals, which form troublesome complexes with thiol (-SH) groups in enzymes and proteins, are toxic to living organisms. The affinity of crown ethers for metals can be increased by altering their structures.

The ion selectivity of benzo-thio crown ether derivatives was systematically assessed against a variety of metal ions in our earlier study (Çalışır and Çiçek 2017). In addition to their high Fe^{3+} selectivity, C1 and C2 were selected due to their distinct structural characteristics, including differences in macrocyclic cavity size (36-crown-8 vs. 42-crown-10) and sulfur-to-oxygen donor atom ratio. These variations provide an opportunity to comparatively evaluate how structural parameters influence metal ion extraction performance. Among the ligands investigated in our previous work, C1 and C2 exhibited the most promising selectivity profile toward Fe^{3+} under competitive conditions, making them suitable candidates for further application-oriented assessment. Among these metal ions were Zn^{2+}, Ag^{+}, Ca^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+}, Co^{2+}, Mg^{2+}, Cd^{2+}, and Ni^{2+}. Under competitive conditions, both C1 and C2 (Fig. 1) showed the highest extraction efficiency towards Fe^{3+}. This pronounced affinity for Fe^{3+} constituted the primary rationale for their selection in the present study. Furthermore, According to HSAB considerations, the presence of both oxygen and sulfur donor atoms provides a balanced coordination environment that may contribute to the observed affinity toward Fe^{3+}. The combined structural features of C1 and C2, together with their previously demonstrated selectivity under competitive conditions, provided the rationale for their further evaluation in real aqueous systems. Finally, C1 and C2's demonstrated coordination compatibility and discrimination ability with

Fe^{3+}, as well as their prior high selectivity in competitive extraction systems, which serve as the methodological foundation for the current work, provide a strong mechanistic and experimental justification for their further study.

Building on these findings, the present study aimed to evaluate the practical applicability of C1 and C2 in real aqueous systems and to test the hypothesis that ligands previously demonstrating high Fe^{3+} selectivity under competitive laboratory conditions would maintain their metal ion extraction efficiency and selectivity in complex environmental water matrices. In order to evaluate their potential contribution to enhancing the quality of potable water, C1 and C2 dissolved in chloroform were used as extractants in liquid–liquid ion-pair extraction experiments using tap and stream water samples. Ion chromatography and Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) were used to determine the initial ion concentrations in the collected samples, and then controlled extraction experiments were carried out. Final ion concentrations were determined by ICP-MS and ion chromatography, and the extraction efficiencies were calculated to quantitatively evaluate ligand performance in real water matrices.

Material and method

Material

The high-purity chemical consumables used in this study were commercially available and did not require any further purification. A Thermo Scientific Smartpure2 ultrapure device provided the pure water that was used for the washing processes. Sigma Aldrich provided the analytical-grade chloroform. A KERN ABJ precision balance with an accuracy of 0.1 mg was used for the weigh-in. The ligands were uniformly dissolved using a Bandolin Sonorex device, and ErgOne and Brand automatic pipettes were utilised for pipetting. An IKA KS 4000i incubator mixer was used to mix the mixture in 50 ml polypropylene Falcon tubes. A Hanna HI 2211 pH metre with an HI1131 probe was utilised to measure the pH. A Mettler Toledo InLab 741 ISM electrode and a Mettler Toledo SevenCompact Conductivity S230 conductometer were used to measure conductivity. A Thermo Scientific Dionex 5000 + ion chromatograph was utilised to measure the concentrations of different ions (K^+, Ca^{2+}, Li^+, NH_4^+, Mg^{2+}, and Na^+ cations; F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, and BrO_3^- anions). The concentrations of additional metal cations were also measured using an ICP-MS device, the Thermo Scientific iCAP Q model with ASX-260 autosampler.

Synthesis of benzo-thio crown ethers

The macrocyclic chemical compounds used in the study (C1 (bis(1,2-dibenzo)octathio tetracarbonyl-36-crown-8) and C2 (bis(1,2-dibenzo)tetrathio tetracarbonyl-42-crown-10) were re-synthesized using the microwave assisted-synthesis method previously developed by Çalışır and Çiçek (Çalışır and Çiçek 2017).

Gathering stream and tap water, analysing the first profile

The study's tap water was obtained from the Central District of Siirt Province (Sample I), the Uludere District of Şırnak Province, (Sample II) and placed in sterile, thiosulfate-free polypropylene plastic bottles (ISOLAB 061.21.250). Ortasu village in the Uludere district of Şırnak province provided the stream water (Sample III), which was collected in ISOLAB 061.21.250 sterile thiosulfate-free polypropylene plastic bottles. The "Water Pollution Control Regulation Sampling and Analysis Methods Communiqué" numbered 27,372, which was published in the Turkish Official Gazette on October 10, 2009, was followed when collecting each water sample. After being collected, water samples were examined within three (3) days. Before being examined, every water sample was kept at +4 °C (Günay 2016). ICP-MS, ion chromatography, a pH metre, and a conductometer were used to measure each water sample's initial ion concentrations. Table 1 lists the analytes, units, and results. In addition, limit regulation values and methods for analyzed parameters were given in Table S1 in Supplementary Information. Metal ions were treated as cationic species in the extraction discussion, while analytical results are reported as total elemental concentrations. Calibration and quantification were performed using commercially available certified multi-element standard solutions. Metals (ions) such as Cd (total), Pb (total) and Li^+, as well as Br^- and BrO_3^- anions, were below the detection limit in all analyzed samples (see Table S1 in the Supplementary Information).

Liquid-liquid ion pair metal extraction

Formulation

The selective transfer of an inorganic reagent from a water-immiscible phase, like water, to an organic phase, like dichloromethane, chloroform, or something similar, is the basis of liquid-liquid ion pair extraction. Briefly, extraction involves the formation of an ion pair between a cationic crown ether complex and the counterion (Fig. 2). During the extraction process (Eq. 1), the species on the left-hand side represent those initially present in the aqueous phase, while

Table 1 Analytical parameters, units, and measured ion concentrations of water samples I–III

Analyte/Parameter*	Units	Analytical results for Samples I–III		
		Sample I	Sample II	Sample III
Sb (total)	μg L^{-1}	0.017 ± 0.002	0.049 ± 0.003	0.672 ± 0.004
As (total)	μg L^{-1}	0.164 ± 0.004	0.269 ± 0.008	0.613 ± 0.000
Cr (total)	μg L^{-1}	1.583 ± 0.016	1.468 ± 0.029	1.503 ± 0.033
Cu (total)	μg L^{-1}	0.742 ± 0.018	0.457 ± 0.009	0.220 ± 0.002
F^-	mg L^{-1}	0.090 ± 0.014	0.116 ± 0.011	0.122 ± 0.007
Ni (total)	μg L^{-1}	1.064 ± 0.013	0.762 ± 0.011	2.934 ± 0.065
NO_3^-	mg L^{-1}	2.381 ± 0.058	2.232 ± 0.179	3.665 ± 0.037
NO_2^-	mg L^{-1}	< LOD	< LOD	0.122 ± 0.003
Cl^-	mg L^{-1}	2.150 ± 0.021	1.020 ± 0.017	2.069 ± 0.010
SO_4^{2-}	mg L^{-1}	14.137 ± 0.139	13.711 ± 0.022	22.459 ± 0.005
Na^+	mg L^{-1}	1.701 ± 0.035	0.707 ± 0.014	1.731 ± 0.003
Fe (total)	μg L^{-1}	393.804 ± 0.037	326.807 ± 5.600	408.425 ± 11.159
Mn (total)	μg L^{-1}	0.431 ± 0.472	0.138 ± 0.010	0.029 ± 0.002
Zn (total)	μg L^{-1}	17.541 ± 1.331	1.712 ± 0.013	0.354 ± 0.032
NH_4^+	mg L^{-1}	< LOD	< LOD	0.050 ± 0.017
K^+	mg L^{-1}	0.413 ± 0.012	0.178 ± 0.004	0.565 ± 0.003
Mg^{2+}	mg L^{-1}	6.882 ± 0.107	10.757 ± 0.011	12.620 ± 0.038
Ca^{2+}	mg L^{-1}	56.704 ± 1.015	49.765 ± 0.054	64.458 ± 0.077
PO_4^{3-}	mg L^{-1}	< LOD	< LOD	0.061 ± 0.005
Se (total)	μg L^{-1}	0.737 ± 0.039	0.382 ± 0.003	1.693 ± 0.028
Mo (total)	μg L^{-1}	0.803 ± 0.012	0.997 ± 0.029	40.831 ± 0.224
B (total)	μg L^{-1}	0.487 ± 0.002	< LOD	< LOD
pH		7.51	7.54	7.61
Conductivity	μS cm^{-1}	337	324	403
Hardness	mg $CaCO_3$ L^{-1}	169.930	168.561	212.921

* Analytes/parameters that could not be detected in the water sample are given in supplementary information Table S2.

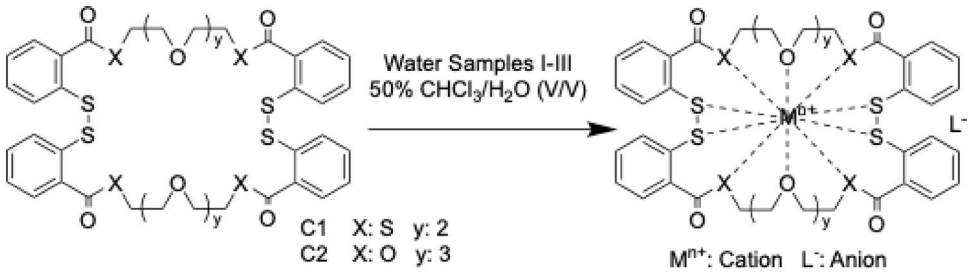

Fig. 2 General illustration of metal complexation

the species on the right-hand side correspond to the ion–ligand complexes formed and transferred into the organic phase. The equilibrium of this extraction can be described by the equilibrium constant K_{ex} (Eq. 2). The concentration of the resulting ion–ligand complex is then calculated according to Eq. 3. Finally, the extraction efficiency (%) is determined using Eq. 4, providing a quantitative measure of the ligand's performance in selectively removing the target ions. This extraction system and equations can be given as follows (Çakır and Çiçek 2004; Çalışır and Çiçek 2017):

$$M^{n+}{}_{(w)} + nA^{-}{}_{(w)} + L_{(w)} \rightleftarrows MLA_{n(Org.)} \quad (1)$$

$$K_{ex} = \frac{[MLA_n]_{Org.}}{[M^{n+}]_{(aq)}\,[L]_{(Org.)}[A^-]^n{}_{(aq)}} \quad (2)$$

$$[MLA_n]_{Org} = [M_0{}^{n+}]_{(w)} - [M^{+n}]_w \quad (3)$$

$$Extraction\ efficiency\ (\%) = \frac{[MLA_n]_{Org.}}{[M_0{}^{n+}]_{(w)}} \quad (4)$$

In here, (M^{n+}) is the metal ion and (A^-) is the counter ion. MLA_n is the ion-pair formed between the metal ion and the counter ion and the crown ether (L) complex (Çakır 1999).

Extraction procedure

A previously developed method was used for liquid-liquid ion pair extraction (Çalışır and Çiçek 2017). The benzo-thio crown ether ligands C1 and C2 were prepared as 10^{-3} M solutions in chloroform prior to the extraction experiments. The reported ligand concentrations of 905.26 ppm for C1

Table 2 Extraction efficiencies (%) of ligands C1 and C2 for ions showing measurable extraction in the natural water samples

Parameter unit	Sample I		Sample II		Sample III	
	C1 (%)	C2 (%)	C1 (%)	C2 (%)	C1 (%)	C2 (%)
Antimony ($\mu g\ L^{-1}$)	0.000	0.000	0.000	0.000	**18.938**	**47.046**
Fluoride (mg L^{-1})	**10.878**	0.000	0.000	**15.354**	**20.689**	0.000
Nickel ($\mu g\ L^{-1}$)	0.000	0.000	0.000	0.000	**23.497**	**29.009**
Nitrate (*mg/L*)	0.000	0.000	0.000	0.000	0.000	**3.322**
Conductivity ($\mu S\ cm^{-1}$)	**3.058**	**13.087**	**4.854**	**4.180**	**10.411**	**6.053**
Sulfate (mg L^{-1})	**0.531**	0.000	**2.500**	**0.430**	**4.837**	**0.850**
Sodium (mg L^{-1})	0.000	0.000	0.000	0.000	**0.075**	0.000
Iron ($\mu g\ L^{-1}$)	**66.582**	**22.717**	**40.582**	**17.231**	**18.644**	**8.563**
Manganese ($\mu g\ L^{-1}$)	**3.730**	**13.871**	0.000	0.000	0.000	0.000
Zinc ($\mu g\ L^{-1}$)	**59.177**	**74.628**	0.000	**74.427**	0.000	**75.083**
Magnesium (mg L^{-1})	0.000	0.000	**1.597**	**2.248**	**4.317**	**2.389**
Calcium (mg L^{-1})	**6.483**	**3.278**	**2.552**	**4.730**	**8.504**	**5.156**
Phosphate (mg L^{-1})	0.000	0.000	0.000	0.000	**8.598**	0.000
Molybdenum ($\mu g\ L^{-1}$)	0.000	**13.028**	0.000	0.000	**1.316**	**1.126**

Note: Values in bold highlight parameters that show significant changes across the conditions studied and are used solely to facilitate visual comparison Bold font does not indicate statistical significance

and 929.10 ppm for C2 were calculated based on the corresponding molecular weights of the compounds. Detailed conversion calculations from molar concentration to ppm units are provided in the Supplementary Information. The same ligand concentration was selected in order to ensure consistency with our previous study, in which identical concentrations were employed for single- and mixed-salt solutions (Çalışır and Çiçek 2017). This approach enables direct comparison of extraction performance between controlled laboratory systems and real water samples. These solutions were used as extractants in the liquid–liquid ion-pair extraction experiments without further modification of concentration during the study. A 50 mL falcon tube (capped plastic tube) was filled with 10 mL of each of the ligand solutions and water samples (Sample I-III). An incubator-shaker was used to shake them for an hour at 300 rpm while maintaining a constant temperature of 25 °C. The solutions were allowed to equilibrate for six to twelve hours after the shaking was stopped. The remaining cation and anion concentrations and extraction percentages were computed after water samples I-III from the aqueous phase were analysed using ICP-MS, ion chromatography, pH metres, and conductometers (Table 2 and Supplementary information (SI), Tables S5-S7).

Instrumentation and analytical conditions

The analytical procedures were structured to clearly distinguish between the techniques used for metal and ionic determinations. Trace elements, including Sb, As, Cd, Cr, Cu, Pb, Ni, Fe, Mn, Zn, Se, Mo, and B, were quantified using inductively coupled plasma–mass spectrometry (ICP-MS). Alkali and alkaline earth metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}), ammonium (NH_4^+), and inorganic anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and BrO_3^-) were determined by ion chromatography (IC).

Instrumental and analytical performance parameters were comprehensively evaluated. Calibration ranges were established using multi-point calibration curves, and correlation coefficients (R^2) were calculated to assess linearity. Calibration was performed using five external standards for ICP-MS and six external standards for ion chromatography.

ICP-MS measurements were reported as total elemental concentrations. The instrument was operated under strong plasma conditions with 1550 W RF power, 15.0 L min^{-1} main argon plasma gas flow, 0.80 L min^{-1} auxiliary gas flow, and 1.01 L min^{-1} jet gas flow. To prevent polyatomic spectral interference, the advanced QCell flat-pole collision/reaction cell was operated in Kinetic Energy Separation (KED) mode at a constant flow rate of 5.0 mL min^{-1}, using high-purity Helium (He) as the collision gas. The following parameters were applied for mass spectrometry data acquisition: 10 scans per integration, 0.025 s dwell time per mass, and a total main run time of 2.5 s per replicate. All samples were measured in triplicate ($n=3$), and analytical results were expressed as mean ± standard deviation (SD) to assess sensitivity. Matrix suppression and instrument drift were mathematically corrected in real-time using In115 as an internal standard sprayed online into the sample stream. All calibration standards were prepared in a matrix of 1% (v/v) suprapur nitric acid (HNO_3). Detailed calibration ranges, correlation coefficients (R^2), and limits of detection (LOD) are given in Tables S3 and S4 in the Supplementary Information.

For ion chramatography method parameters: Software: Chromeleon, Dedector: Conductivity dedector, Suppressor

type (cation): CSRS_4 mm (60 mA), Suppressor type (anion): ASRS_4 mm (112 mA), Column and compartment tempetature: 30 °C, Dedector cell tempetature: 30 °C, Flow rate: 1.0 mL min^{-1}, Eluent formation: Generated eluent generator system, Eluent generated mode: Gradient (from 12 to 45 mM), Column and guard column type (anion): Dionex IonPac AS11-HC column (4 × 250 mm) and IonPac AG11-HC guard column (4 × 50 mm); Column and guard column type (cation): Dionex IonPac CS12A column (4 × 250 mm) and IonPac CG12A guard column (4 × 50 mm), Injection volume: 10 µL (BrO_3^-: 50 µL), Sample filtration: 0.45 µm PTFE filter), Run time: 44 min .The eluent was generated electrolytically using potassium hydroxide (KOH), with a gradient ranging from 12 to 45 mm. Methanesulfonic acid (MSA) at a concentration of 18 mM used as the eluent.

Results and discussion

As part of this study, the liquid–liquid ion-pair extraction method was applied to remove selected cations and anions from tap and stream water samples (Samples I–III). Prior to extraction experiments, the raw water samples were comprehensively analyzed to determine their initial physicochemical properties. All measured parameters of Sample I (tap water) were found to be within acceptable limits (Supplementary information (SI), Table S1). Sample III showed higher conductivity values, higher concentrations of several elements (Fe, Mo, Ca^{2+}, Sb, and As), and higher concentrations of various anions (SO_4^{2-}, Ni^{2+}, and NO_3^-), compared with Samples I and II. The relatively high chemical load in Sample III may be associated with the geographical characteristics of the region, which is located within mining and coal basin areas. Br^- and BrO_3^- ions were also analysed; however, both species were below the detection limit in all samples and are therefore reported as <LOD in the results tables.

Ion-pair liquid–liquid extraction experiments were subsequently performed on Samples I–III. The remaining ion concentrations after extraction (Supplementary information (SI), Tables S5-S7) and corresponding extraction efficiencies (%) are summarized in Table 2. To ensure high complexation rates of C1 and C2 benzo-thio-crown ethers, high-concentration solutions were prepared in chloroform. Equal volumes of water samples and ligands were combined under laboratory conditions to investigate the removal behavior of selected cations and anions.

A slight increase in pH was observed after the extraction process for all water samples (Supplementary information (SI), Tables S5-S7). After treatment with the crown ether ligands the pH values in Sample I changed from 7.51 to 7.66–7.80, in Sample II from 7.54 to 7.80, in Sample III from 7.61 to 7.72–7.74. This slight pH increase is most likely related to changes in aqueous equilibrium conditions after partial removal of iron, manganese (partially), antimony, etc. some types of hydrolyzable metals, which was present in relatively higher concentrations in the samples under investigation and was partially extracted during the treatment process (Table 2) (Díaz Gutiérrez et al. 2023; Kang et al. 2022; Loughlaimi et al. 2024; Suiyi et al. 2023; Yuxin et al. 2023). Dissolved Fe species are easily hydrolysed in aqueous systems, generating protons and leading to lower pH values (Stumm and Morgan 1995; Langmuir 1997). Therefore, partial removal of iron species may shift these equilibria toward lower proton generation, resulting in a modest increase in pH.

Moreover, the ion-pair extraction process may also cause small shifts in the solution equilibria by partial removal of the accompanying counter anions such as sulphate, phosphate and nitrate species which may affect the overall ionic balance of the aqueous phase. The decrease in conductivity values after extraction further supports a decrease in the total dissolved ionic content. Small variations in ionic strength are known to influence ion activity coefficients and may therefore contribute to minor variations in measured pH values in multicomponent aqueous systems (Skoog et al. 2013; Shirazi et al. 2025; Stumm and Morgan 1995). Also, minor contributions of dissolved inorganic carbon equilibria during mixing and phase contact at the aqueous/organic interface cannot be completely ruled out (Stumm and Morgan 1995; Langmuir 1997). Given the relatively minor magnitude of the pH shift observed, these effects should be interpreted as minor equilibrium shifts caused by the extraction process, rather than a significant shift in overall water quality.

The ion-pair extraction mechanism proposed in this study is supported by qualitative trends rather than stoichiometric or equilibrium-based quantitative calculations. Since no detailed speciation or mass balance modeling was performed, the mechanistic interpretation is based on observed decreases in dissolved ion concentrations and conductivity changes after treatment (Supplementary information (SI), Tables S5-S7). The relatively moderate reduction in ionic content (change in conductivity = ~ 3–13%) suggests that the extraction process is consistent with selective ion association rather than complete bulk phase removal.

Even though the water quality parameters of Sample I fall within the acceptable limits for drinking water, the sample was subjected to extraction using C1 and C2 ligands to evaluate the ion-binding behavior of the synthesized crown ether derivatives. Fluoride and sulphate anions were extracted by the C1 ligand, whereas none of the investigated anions were extracted by the C2 ligand according to the results presented in Table 2. In contrast to the anions, calcium, zinc,

iron, and manganese species (reported as total elemental concentrations) were extracted by both C1 and C2 ligands. Among the investigated ions, the C1 ligand removed total iron (66.582%) and zinc (59.177%) species from Sample I more efficiently than the other ions. In contrast, the C2 ligand showed its highest extraction efficiency toward zinc species, removing 74.628% of Zn from the aqueous phase. These results indicate the formation of metal–ligand complexes followed by partial transfer of these complexes into the organic phase. In ion-pair extraction systems, anions may accompany the extracted metal complexes as counterions. The decrease in conductivity observed after extraction with both ligands indicates that certain ions were removed from the aqueous phase. In addition, the pH increased slightly after treatment, resulting in a modest improvement in the water quality parameters. The decreases in calcium and magnesium concentrations also suggest a partial reduction in water hardness.

The application of C1 and C2 ligands to Sample II resulted in observable improvements in water quality parameters, including a slight reduction in water hardness, an increase in pH, and a decrease in conductivity (Table 2). Sulfate (SO_4^{2-}) anions were also found to decrease in concentration after extraction with both ligands, whereas fluoride (F^-) ions decreased only in the presence of C2. As discussed above, these anions are not directly complexed by the ligands but are likely co-extracted as counterions accompanying the metal–ligand complexes during the ion-pair extraction process. In addition to these anions, both ligands were capable of extracting total calcium, magnesium, and iron species from the sample. Among the investigated cations, C2 exhibited the highest extraction efficiency toward zinc species, removing 74.427% of Zn from the aqueous phase. The approximately 4% decrease in conductivity indicates a reduction in the overall dissolved ionic content of the sample, which can be attributed to the removal of both cations and their accompanying counter anions during the extraction process.

A water sample referred to as Sample III was treated with the synthesized benzothiocrown ether derivatives to evaluate their ability to remove specific ions (Table 2). Both crown ether ligands showed extraction toward several metal species, including antimony (Sb), nickel (Ni), total iron species, magnesium (Mg^{2+}), calcium (Ca^{2+}), and molybdenum species (reported as total Mo). A decrease in sulfate (SO_4^{2-}) concentration was also observed for both ligands, which is most likely associated with its co-extraction as a counterion accompanying the metal–ligand complexes during the ion-pair extraction process. The C1 ligand additionally led to decreases in phosphate (PO_4^{3-}), sodium (Na^+), and fluoride (F^-) concentrations, whereas the C2 ligand showed selectivity toward zinc (Zn^{2+}) and nitrate (NO_3^-), achieving a zinc extraction efficiency of 75.083%.

Upon examining all the water samples, the C1 ligand consistently removed total iron, calcium (Ca^{2+}), and sulfate (SO_4^{2-}) ions across all samples. In contrast, the C2 ligand extracted total iron, zinc species, and calcium (Ca^{2+}) ions, thereby improving the overall quality of the water samples. Notably, the concentrations of antimony (total Sb) and nickel (total Ni) in the stream water (Sample III) were higher than those in the tap water samples. The complexing agents were therefore able to remove a portion of these elemental species, further enhancing water quality. Additionally, they extracted other components such as phosphate (PO_4^{3-}) and magnesium (Mg^{2+}), which were present at higher levels in the stream water (Sample III) compared to the tap water samples (Sample I–II).

In addition to these findings, examination of the extraction results together with the conductivity measurements of the water samples (determined by conductometry) revealed a decrease in the total dissolved ionic content ranging from 3 to 13%. The crown ether compounds did not remove many of the highly concentrated cations and counter-anions; instead, they selectively targeted parameters that negatively affect water quality. Despite their relatively low concentrations, the removal of more toxic metals—such as total iron, total zinc, total antimony (Sb), total molybdenum (Mo), and total nickel (Ni)—while leaving largely unchanged the cations essential for living organisms is consistent with the conductivity data. This observation highlights the selective affinity of the ligands toward specific metal species.

The experimental results also indicate that anions were not the primary targets of the extraction process. The observed decreases in anionic concentrations are attributed to ion-pair formation, in which anions accompany the extracted metal cations to maintain charge neutrality rather than being directly complexed by the ligands. In liquid–liquid ion-pair extraction systems, this mechanism involves the association of the cation–crown ether complex with its counterion in solution, enabling the transfer of the ion pair into the organic phase.

According to Lewis acid-base theory, anions and cations are categorized as hard, soft, or borderline (moderate) (Cicek and Calisir 2016). When the extractive behavior of C1 and C2 crown ethers was evaluated across all water samples, it was found that they generally removed cations such as Fe, Mn, Mo, Sb, Ni, and Zn species (reported as total elements measured by ICP-MS), Ca^{2+}, Mg^{2+}, species (measured by IC), as well as anions including F^-, PO_4^{3-}, SO_4^{2-}, and partially NO_3^- (Table 2). Literature sources indicate that Fe^{3+}, Mn^{2+}, Mo species, Ca^{2+}, and Mg^{2+} are classified as hard Lewis acids, whereas Zn^{2+} and Ni^{2+} are considered borderline acids (see in Table S8 in the Supplementary Information).

Similarly, fluoride, phosphate, sulfate, and nitrate are hard Lewis bases (Leach 1999; Vigneresse 2009). According to Pearson's Hard and Soft Acids and Bases (HSAB) principle, hard acids tend to form complexes with hard bases, while soft acids prefer soft bases (Pearson 1968). The benzocrown ether derivatives used in this study contain functional groups such as ether bridges, benzene rings, and carbonyl groups, which exhibit hard Lewis base character. They also include sulfur atoms (disulfide and thioester) that exhibit soft acid characteristics. Both C1 and C2 contain benzene rings, ether and ester/thioester groups, and disulfide bonds. The main structural difference is that C1 contains a thioether functionality but fewer ether bridges, whereas C2 contains a higher number of ether bridges together with an ester group, suggesting that C2 should behave as a relatively harder Lewis base. However, the results show that although both compounds efficiently extract the relatively hard Fe^{3+} ion, C1—despite being comparatively less hard—exhibited higher extraction efficiencies in all water samples. In contrast, the borderline Zn^{2+} ion was extracted more effectively by C2, the relatively harder Lewis base. A similar tendency was observed for total Sb, Mn^{2+}, Mg^{2+}, Ca^{2+}, Ni^{2+}, and total Mo species. F^{-}, PO_4^{3-}, SO_4^{2-}, and partially NO_3^{-} ions — being hard Lewis bases—were likely co-extracted as ion pairs with the corresponding hard Lewis acids. This behavior is consistent with ion-pair extraction, where the removal of cations from the aqueous phase is accompanied by the extraction of counter anions in order to maintain overall charge neutrality. Although intrinsic base character plays a decisive role, the number of ether bridges significantly enhances hard base behavior. Specifically, C1 contains three ethylene glycol ether bridges, whereas C2 contains four, increasing C2's affinity toward hard Lewis acids. Additionally, each compound contains four benzene rings, further contributing to donor strength. An increase in the number of ether donor sites correlates with enhanced extraction of cations exhibiting hard Lewis acid character. These findings support the interpretation that the ions removed from the water samples predominantly fall within the hard Lewis acid–base classification.

In addition to the ions showing measurable extraction (Table 2), several dissolved species present in the original water matrices did not exhibit any detectable extraction with either ligand (Supplementary information (SI), Tables S5–S7). These include elements such as arsenic, chromium, copper, selenium, and boron, as well as major ions such as potassium and chloride, whose concentrations remained unchanged after the extraction process within experimental uncertainty. In some cases, the ions were present in the original samples but no measurable decrease in concentration was observed after treatment, indicating that they were not significantly complexed by the ligands under the applied conditions. The absence of extraction for these species can be attributed to the limited affinity of the benzothiocrown ether ligands toward these ions. According to the Lewis acid–base interaction concept, the relatively hard character of several of these ions results in weaker interactions with the sulfur-containing donor atoms present in the ligand framework. In addition, the size and coordination preferences of certain ions may not be compatible with the cavity geometry of the crown ether structures. Consequently, these ions remain predominantly in the aqueous phase during the ion-pair extraction process.

In addition to the HSAB considerations discussed above, the size compatibility between the metal ion and the crown ether cavity may also influence the extraction behavior. Crown ethers are relatively rigid macrocyclic structures, and therefore the ionic radius of the metal ion can play an important role in complex formation. In our previous work, the extraction behavior of similar metal ions was evaluated by considering both the HSAB concept and the relationship between ionic radius and ligand hardness parameters derived from HOMO–LUMO energy gaps. Those results indicated that metal ions with ionic radii compatible with the effective coordination environment of the crown ether framework exhibited enhanced extraction efficiencies (Cicek and Calisir 2016). However, it should be noted that the present study was conducted using natural water samples containing multiple competing ions. Under such complex aqueous conditions, the extraction selectivity cannot be attributed solely to ionic radius matching, but rather to a combined effect of Lewis acid–base interactions, ionic size compatibility, and competitive complexation equilibria occurring in the solution phase. Therefore, the extraction trends observed for C1 and C2 likely reflect the interplay between HSAB preferences and size-related coordination effects of the crown ether cavity (Pearson 1988).

The effective ionic radii of the investigated metal ions (0.65–1.00 Å) are provided in Table S8 in the Supplementary Information. These values fall within the range in which coordination with crown ether cavities is feasible, particularly for larger macrocyclic environments, suggesting that both ionic size compatibility and HSAB interactions contribute to the observed extraction behavior (Shannon 1976; Pedersen 1967; Pearson 1968).

In addition to HSAB considerations, the size compatibility between the metal ion and the crown ether cavity may also influence the extraction behavior (Bond et al. 2000). Crown ethers are relatively rigid macrocyclic structures possessing well-defined cavity dimensions. Therefore, the interaction strength between a metal ion and the macrocyclic ligand depends not only on Lewis acid–base interactions but also on the relationship between the ionic radius of the metal ion and the cavity size of the crown ether (Yoshizuka et al.

2026; Yu et al. 2015). When the ionic radius of a metal ion is compatible with the cavity environment of the ligand, more stable host–guest complexes can form, which enhances the extraction efficiency. However, because the present experiments were carried out using natural water samples containing multiple competing ions, the observed extraction trends likely result from the combined effects of Lewis acid–base interactions, ionic size compatibility, and competitive complexation equilibria in solution.

The selectivity observed for C1 and C2 ligands can be further interpreted by considering the combined effects of ligand rigidity, cavity dimension compatibility, and metal ionic radius matching. Crown ether–type macrocyclic structures exhibit host–guest recognition behavior in which complex formation is strongly influenced by the geometric and electronic compatibility between the ligand cavity and target metal ions (Ariga and Kunitake 2006; Ray et al. 2025). In this context, the relatively smaller and more flexible cavity environment of C1 appears to favor complexation with smaller hard Lewis acid species such as Fe^{3+}, which is consistent with its higher iron extraction efficiency across the analyzed water samples. Conversely, the presence of a larger number of ether bridges in C2 increases macrocyclic rigidity and expands the effective cavity environment, promoting stronger interactions with borderline metal ions, particularly Zn^{2+}, whose ionic radius is more compatible with the structural dimensions of C2. This interpretation is also consistent with HSAB theory. Therefore, the extraction behavior of the synthesized crown ether derivatives can be rationalized through a synergistic consideration of ligand structural rigidity, cavity size effects, and ionic radius matching principles.

A closer examination of the investigated ions also supports the proposed size–selectivity relationship. Among the studied metal ions, Fe^{3+} possesses one of the smallest ionic radii among the investigated ions (0.65 Å) and behaves as a hard Lewis acid, which is consistent with its efficient extraction by the relatively smaller cavity environment of the C1 ligand. Similarly, Mg^{2+} (0.72 Å) and Ni^{2+} (0.69 Å) fall within a comparable size range and may interact favorably with oxygen donor atoms of the crown ether through hard or borderline acid–base interactions. In contrast, Ca^{2+} exhibits a larger ionic radius (1.00 Å), which is closer to the upper limit of the investigated size range and may therefore benefit from more flexible macrocyclic environments capable of accommodating larger ions. The relatively efficient extraction of Zn^{2+} (0.74 Å), a borderline Lewis acid, particularly by the C2 ligand, may be associated with the larger and more rigid cavity environment created by the increased number of ether bridges in this macrocycle. Similarly, Sb^{3+} (~0.76 Å) and Mo species (reported as total Mo, ~0.69 Å) fall within the same general ionic radius window, suggesting that their extraction behavior may arise from a combination of ionic radius compatibility and competitive coordination equilibria present in the multi-ionic natural water matrices.

Crown ethers are well known supramolecular hosts capable of selectively binding metal ions through size matching between the ionic radius of the metal and the cavity of the macrocycle. Because of this selective recognition ability, crown ether derivatives have attracted increasing attention for the separation and recovery of specific metal ions from aqueous environments (Liu et al. 2025; Lin et al. 2024). Recent studies have shown that crown ether functionalities can be incorporated into various materials such as hydrogels, membranes, and nanofiltration systems to enhance ion selectivity in water treatment processes (Li et al. 2026). For example, crown-ether-based adsorbent systems have demonstrated high selectivity for specific cations due to the host–guest interactions within the macrocyclic cavity, which is governed by the compatibility between ionic radius and cavity size (Chen et al. 2024; Lin et al. 2024). Likewise, crown ether-modified membranes have recently been developed for selective ion separations such as Li^{+}/Mg^{2+} and radionuclide removal in aqueous systems (Yin et al. 2024; Mamardashvili et al. 2021; Wang and Zhuang 2017). These findings indicate that macrocyclic ligands can serve as selective recognition units when integrated into separation materials.

In this context, the present work should be considered as a proof-of-concept investigation evaluating the ion-binding and extraction behavior of the synthesized crown ether ligands in complex natural water matrices. Batch extraction experiments were therefore employed as an initial screening approach to evaluate ion recognition and selectivity under environmentally relevant conditions. Although conventional large-scale water purification technologies such as precipitation, adsorption, or membrane filtration remain more economical for bulk water treatment, supramolecular ligands such as crown ethers offer a unique advantage in selective ion recognition and targeted removal of specific metal ions (Lin et al. 2024; Mamardashvili et al. 2021). Therefore, these systems may find applications in selective separation, analytical preconcentration, or advanced hybrid purification systems where high ion selectivity is required.

Conclusion

This study demonstrated that C1 and C2 compounds, derivatives of benzo-crown ethers, primarily target specific metal cations, while anionic species may be co-transported as counter ions during ion-pair complexation from aqueous media through Lewis acid–base interactions and complexation mechanisms. Unlike traditional chemical precipitation

methods, this process relies on Lewis acid-base interactions and complexation mechanisms, enabling targeted removal of ions that negatively impact water quality, even when present at low concentrations. Post-treatment conductivity measurements revealed a reduction in total dissolved ions ranging from 3% to 13%. The ligands showed higher affinity toward toxic or environmentally undesirable metal species such as Fe^{3+}, Zn^{2+}, Sb^{3+}, Mo species (reported as total Mo by ICP-MS), and Ni^{2+}. Many of these ions are classified as "hard" or "borderline" acids according to Lewis acid-base theory and exhibit high affinity for the functional groups of the crown ether compounds used, particularly ether bridges and benzene rings. Although compound C1 has a relatively less hard Lewis base character due to its fewer ether groups and the presence of a thiother group, it removed the Fe^{3+} ion with higher efficiency in all samples. On the other hand, compound C2, which has more ether bridges and one ester group, showed higher selectivity towards the Zn^{2+} ion and also exhibited in the extraction of other metal ions such as Sb^{3+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, and Ni^{2+}. The simultaneous decrease in the concentrations of certain anions, including F^-, PO_4^{3-}, SO_4^{2-}, and to some extent NO_3^-, supports the occurrence of ion-pair formation accompanying the extraction of metal–ligand complexes. Overall, the results indicate that the number and nature of donor groups within the macrocyclic structure play a key role in determining ligand affinity toward hard Lewis acid species. These structure–function relationships highlight the potential of benzo-crown ether derivatives as tunable molecular tools for selective ion recognition and targeted removal of toxic metal ions from complex aqueous matrices.

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Declarations

Conflict of interest The authors declare no conflict of interests.

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