Journal of Inclusion Phenomena **6** (1988), 57–64.

Extraction of Co(II) and Ni(II) Ammine Cations from Aqueous Solutions into Chloroform by Highly Lipophilic Crown Carboxylic Acids

JERZY STRZELBICKI and A. CHAREWICZ
Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wroclaw, 50-370 Wroclaw, Poland

RICHARD A. BARTSCH
Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-4260, U.S.A.

(Received: 27 March 1987; in final form: 10 May 1987)

Abstract. The proton-ionizable crown ethers, 2-[(*sym*-dibenzo-14-crown-4)oxy]-decanoic acid (**1**), 2-[*sym*-dibenzo-16-crown-5)oxy]decanoic acid (**2**), and 2-[*sym*-dibenzo-19-crown-6)oxy]decanoic acid (**3**) efficiently extract Co(II) and Ni(II) ammine cations from highly alkaline aqueous solutions ($pH > 10$) into chloroform. For extractions of the individual metal species, **2** is more efficient than **1** or **3**. In competitive extraction systems, good selectivity for Co(II) ammine cations over Ni(II) ammine cations is observed.

Key words: Solvent extraction, crown carboxylic acids, Co(II) and Ni(II) ammine cations.

1. Introduction

The potential of crown ethers (macrocyclic polyethers) as specific metal ion extractants [1–3] was markedly enhanced by the introduction of crown ethers which bear pendant ionizable groups [4–8]. The combination of ion binding cavities which possess fixed dimensions and pendant ionizable groups creates novel bifunctional complexing agents.

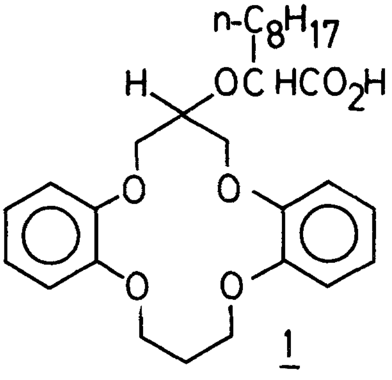
A distinct advantage of such ionizable crown ethers compared with the more ordinary neutral crown ethers is that transport of a metal cation from the aqueous phase into an organic medium does not require simultaneous transfer of an aqueous phase anion.

Ionizable crown ethers have been utilized as mobile carriers of alkali and alkaline earth cations in liquid-liquid extraction and liquid membrane permeation processes [1, 3, 7–24]. In comparison, extraction and transport of transition metal cations by ionizable crown ether compounds have received much less attention [15, 25, 26]. An investigation of the solvent extraction of Co(II) and Ni(II) cations from aqueous phases into chloroform by lipophilic crown carboxylic acids **1–3** has now been undertaken to probe the influence of systematic polyether cavity size variation upon the complexation of such closely-related transition metal cations.

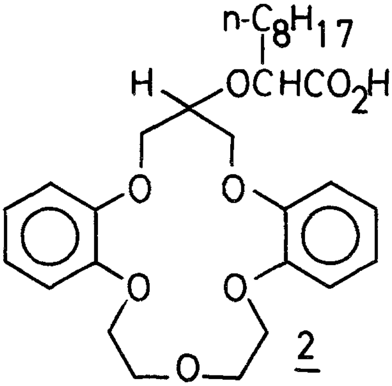
2. Experimental

2.1. MATERIALS AND REAGENTS

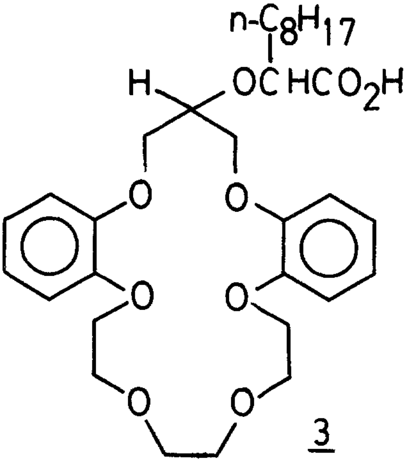
Crown carboxylic acids **1–3** were prepared by the published procedures [8, 23, 27].



1



2



3

Reagent grade dimethylglyoxime, chloroform, $NiCl_2 \cdot 6H_2O$, $CoCl_2.H_2O$, hydrochloric acid, ammonium hydroxide, ammonium chloride, ammonium citrate, and iodine were obtained from POCh (Gliwice, Poland) and SLX-31 liquid scintillation cocktail was obtained from Tesla (Prague, Czechoslovakia). All aqueous solutions were prepared using doubly-distilled water. Radioactive isotopes ^{58}Co and ^{63}Ni (as aqueous chlorides) obtained from IBJ (Swierk, Poland) were carrier-free or of sufficiently high specific radioactivity.

2.2. APPARATUS

Concentrations of cobalt in the aqueous and organic phases were determined radiometrically (^{58}Co) with a Nuclear Data (Model 1200) multichannel gamma radiation spectrometer and a Canberra Industries (Model 7228) semiconductor probe while concentrations of nickel in the organic phases were determined by means of a liquid scintillation radiometrical technique (^{63}Ni) with a ZZUJ 'Polon' (Warsaw) single channel counting system. Equilibrium pH measurements in the aqueous phases were made with an Elpo (Model N512) pH meter and a Energopomiar (Model SAgP-209W) glass body combination electrode. Absorption spectra of the organic phases were measured with a Hitachi (Model 356) ultraviolet spectrophotometer and a Zeiss (Jena) Specord 75 infrared spectrophotometer.

2.3. PROCEDURE

Liquid-liquid extractions were conducted at room temperature (20–23 °C). The organic phase (5 mL) containing the crown ether carboxylic acid (0.010 M) in chloroform and an aqueous solution (5 mL) of cobalt and/or nickel chlorides (0.0050 M each, labeled with ^{58}Co and ^{63}Ni radioisotopes) were placed into a set of separatory funnels. To adjust the equilibrium pH of the aqueous phase, NH_4Cl and NH_4OH were added at various molar ratios to give a total ammonium salt concentration of 2.40 M. The separatory funnels were shaken vigorously for 15 min and then allowed to stand for 20 h to provide complete separation of the organic and aqueous phases. Samples (1.00 mL) of each phase were removed for the γ-spectrometric determination of cobalt concentrations. Samples (0.025 mL) of each phase were also removed for determination of nickel concentrations by liquid scintillation counting. Additional samples (0.50 mL) of the aqueous phases were removed to determine the nickel concentrations colorimetrically. The absorbance of the organic phase was measured at 273–274 nm after dissolving 0.50 mL of the organic phase in 9.50 mL of chloroform. Finally, the equilibrium pH of the aqueous phase was measured.

3. Results and Discussion

Crown carboxylic acids **1**–**3** are a series of closely-related ionizable crown ethers in which the polyether ring size is systematically varied from 14-crown-4 to 16-crown-5 to 19-crown-6, respectively.

In initial experiments, 0.010 M aqueous solutions of Co(II) or Ni(II) chlorides to which HCl or NaOH had been added as a pH regulator were extracted with 0.010 M solutions of **1** or **2** in chloroform. No metal cation transfer into the organic phase from acidic aqueous solutions was noted and stable metal hydroxide precipitates formed in the extraction system for neutral and alkaline aqueous solutions. To circumvent such problems, aqueous ammonia solutions of Co(II) and Ni(II) chlorides were used as the aqueous phases for subsequent extraction experiments. It has been determined [28] that Co(II) and Ni(II) exist in aqueous ammonia as $[M(NH_3)_n]^{2+}$ where n may vary from 1 to 6. Under the experimental conditions which were utilized in this study, the concentrations of free Co(II) and Ni(II) cations in the aqueous phases would not exceed 2.36×10^{-10} and 5.54×10^{-14} M, respectively.

Results for the extraction of 0.0050 M Ni(II) ammine cations from aqueous solutions into 0.010 M chloroform solutions of **1**–**3** are presented in Figure 1. For all three crown carboxylic acids, extraction of Ni(II) into the organic phase is negligible until the equilibrium pH of the aqueous phase exceeds 10. The maximum values for the fraction of metal cations extracted (R) are influenced by variation of the polyether ring size and decrease in the order **2**(63%) > **1**(43%) > **3**(25%).

Analogous data for the extraction of 0.0050 M Co(II) ammine cations are shown in Figure 2. The fraction of Co(II) extracted is low in the region of pH = 8–10 and

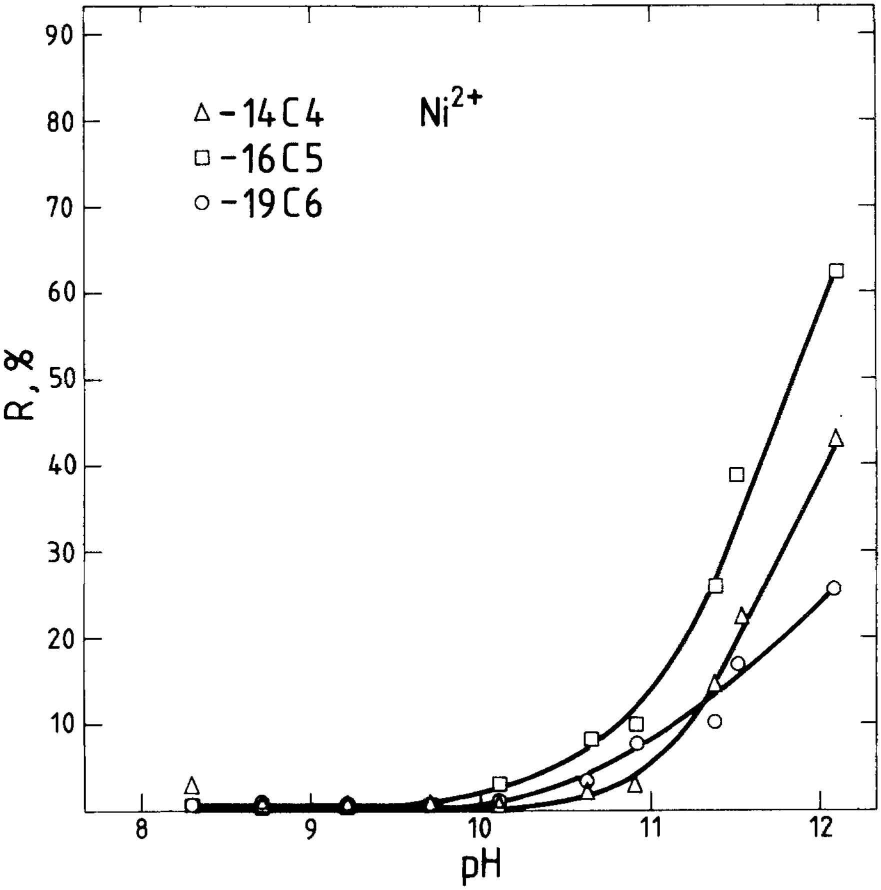


Fig. 1. %(*R*) of nickel extracted from aqueous ammonia solutions of 0.0050 M Ni(II) chloride into 0.010 M solutions of crown carboxylic acids in chloroform vs. the equilibrium pH of the aqueous phase.

increases rapidly as the pH exceeds 10. Maximal *R* values are 86, 77 and 74% with **2**, **1** and **3**, respectively.

When the crown carboxylic acids were replaced with octanoic acid or dodecanoic acid and the extractions of 0.0050 M Ni(II) or Co(II) ammine cations were attempted under the conditions cited above, no metal cation transfer to the organic phase could be detected. Hence the essential nature of the polyether portions of ligands **1–3** is established.

Results for competitive extractions of Ni(II) and Co(II) ammine cations from aqueous solutions in which the initial concentration of each metal chloride was 0.0050 M by 0.010 M solutions of **1–3** are given in Figures 3a–c, respectively. Substantial selectivity for extraction of Co(II) over Ni(II) is readily evident. At an aqueous phase pH of 12, the Co(II)/Ni(II) concentration ratios in the organic phases are 7.3, 6.6, and 5.3 for **1–3**, respectively.

To probe for possible losses of the ionizable crown ether extractants from the chloroform phases during extraction, ultraviolet absorption spectra of both media at 273–274 nm (absorption maxima for the crown carboxylic acids) were measured. Organic phase absorptions at this wavelength were constant or increased somewhat

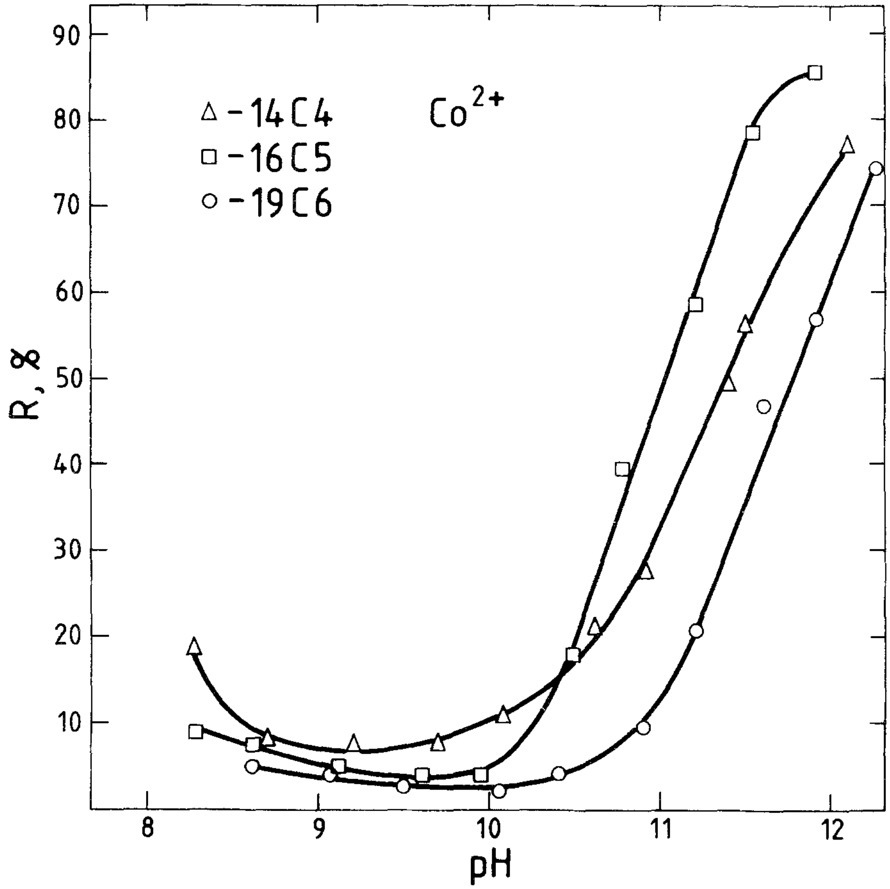


Fig. 2. %(R) of cobalt extracted from aqueous ammonia solutions of 0.0050 M Co(II) chloride solutions into 0.010 M solutions of crown carboxylic acids in chloroform vs. the equilibrium pH of the aqueous phase.

as the organic phase metal ion concentration increased. Aqueous phase absorptions were negligible at this wavelength which verified that the extractants were sufficiently lipophilic to avoid any measurable loss from the chloroform phase during extraction.

To obtain insight into the stoichiometry of the extraction complex, single ion extractions of Co(II) ammine cations from 0.010 M aqueous solutions with 0.010 M solutions of **1–3** in chloroform were conducted at an equilibrium pH of 12.0. The fractions of Co(II) which were transferred into the organic phase increased from 40% for **2** and **3** to 50% with **1**. Since the minimum value of the organic phase concentration ratio of crown carboxylic acid to metal cation is 2.0, an extraction complex stoichiometry of $M(NH_3)_x^{2+} \cdot 2(\text{crown carboxylate}^-)$ is indicated. Presumably strong hydration of Cl^- prevents its participation in the extraction complex.

Specific complexation behavior of crown ethers towards simple cationic species is most commonly rationalized in terms of the cation and polyether cavity ratios [29, 30]. From an examination of Corey–Pauling–Kortun (CPK) space filling models, the polyether cavity diameters for **1–3** are estimated to be 1.2–1.5, 2.0–2.4 and 3.0–3.5 Å, respectively [18], while the ionic diameter for Co(II) is 1.48 Å and for Ni(II) is 1.44 Å [31]. Diameters of the Co(II) and Ni(II) ammine cations may be

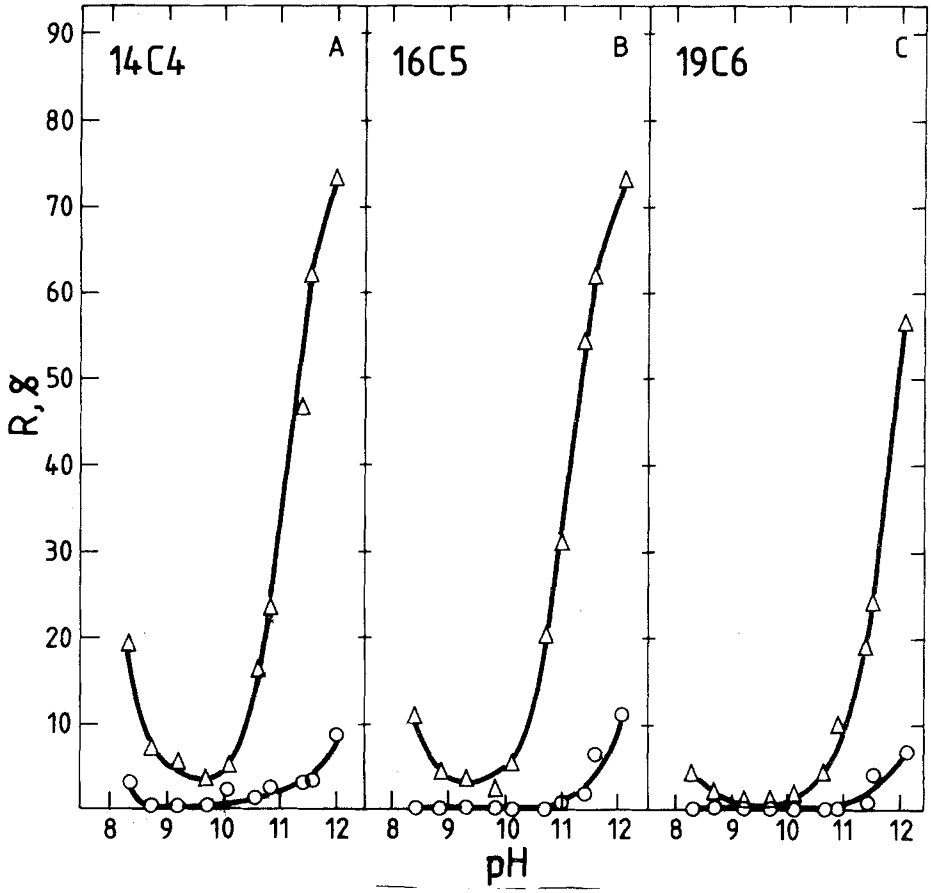


Fig. 3. %(R) of metal extracted into the chloroform phase vs. the equilibrium pH of the aqueous ammonia phase for competitive extractions of 0.0050 M Co(II) and 0.0050 M Ni(II) chlorides by 0.010 M crown carboxylic acids (Δ = cobalt, ○ = nickel).

estimated using the Co—N (2.00 Å) and Co—Cl (2.33 Å) bond lengths determined for the $[Co(NH_3)_{6-n}Cl_n]^{(3-n)+}$ cations [32] and the N—H (1.10 Å) bond length and H—N—H bond angle of 106.7° determined for ammonia [33]. Estimated in this way, the diameter of the $Co(NH_3)_6^{3+}$ cation is 5.1 Å. Taking into consideration the differing ionic diameters for Co(III), Co(II) and Ni(II) cations [31], the diameters of $Co(NH_3)_6^{2+}$ and $Ni(NH_3)_6^{2+}$ cations are estimated to be 5.5 and 5.4 Å, respectively. Thus, for both the cations themselves and their hexaammino complexes, the Co(II) and Ni(II) species are anticipated to have very similar steric dimensions.

Extraction of Co(II) and Ni(II) from aqueous ammonia solutions into chloroform by ligands **1**–**3** is appreciable only under quite alkaline conditions ($pH > 10$) for which the crown ether carboxylate form would predominate. With an apparent extraction complex stoichiometry of $M(NH_3)_x^{2+} \cdot 2(\text{crown carboxylate}^-)$, the ionized form of the extractant would provide the requisite anions for electroneutrality.

The presence of $Ni(NH_3)_6^{2+}$ ammine cations in the organic phase after extraction of aqueous ammonia solutions of Ni(II) by chloroform solutions of **1**–**3** was established by the observed infrared absorption maxima at 3330 and 3230 cm^{-1} for **1** and **2** and at 3330 and 3270 cm^{-1} for **3** [34]. In the cobalt system, absorption maxima were noted at 3280, 3245, and 3158 cm^{-1} for **1**, at 3295, 3198, and 3163 cm^{-1} for **2** and at 3265 and 3198 cm^{-1} for **3** which verifies the presence of both $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ cations [34]. Presumably the latter species was formed by facile air oxidation of the former in the aqueous ammonia-chloride media [35].

Structures of several crown ether complexes with transition metal ammine cations have been determined by X-ray diffraction [36–40]. In all cases, the crown ether second-sphere ligands [40] are hydrogen bonded to ammine ligands in the first coordination sphere of the transition metal. By analogy with this structural information and an apparent stoichiometry of $M(NH_3)_x^{2+} \cdot 2(\text{crown carboxylate}^-)$ in the present study, it is proposed that the extraction complex is a sandwich-type complex in which the Co(II) or Ni(II) ammine cation is situated between two crown ether carboxylate anions. Strong hydrogen bonding of the ammine ligands with the cyclic polyethers would stabilize the complex.

In the single ion experiments, crown carboxylic acid **2** provides better extraction of Co(II) and Ni(II) from highly alkaline aqueous ammonia solutions than does **1** or **3**. Examination of CPK space-filling models suggests that three point hydrogen-bonding of a coordinated ammine ligand with the polyether ring oxygens of **2** would be more favorable than in **1** or **3**.

The observed selectivity for extraction of Co(II) ammine cations in the competitive experiments indicates that extraction efficiency may depend upon the stereochemical preference and flexibility of the metal ammine cation. Although Ni(II) exhibits a strong preference for octahedral coordination, Co(II) readily shifts from octahedral to tetrahedral (or intermediate) coordination geometries. Stereochemical flexibility within the Co(II) ammine complex could be very helpful in enhancing the strength of the hydrogen-bonding interactions of the first-sphere ammine ligands with the second-sphere crown ether carboxylate ligands.

Acknowledgements

The authors would like to thank Dr Andrzej T. Kowal for measurement and interpretation of the infrared spectra and Dr Robert A. Holwerda for helpful discussions. This research was supported by the Committee of Chemical Sciences of the Polish Academy of Sciences (for J.S. and W.A.C.) and by the Division of Basic Chemical Science of the United States Department of Energy (Contract DE-AS05-80ER10604) for R.A.B.).

References

1. Y. Marcus and L. E. Asher: *J. Phys. Chem.* **82**, 1246 (1982).
2. I. H. Gerow and M. W. Davis: *Sep. Sci. Technol.* **14**, 395 (1979).
3. I. H. Gerow, J. E. Smith, Jr., and M. W. Davis, Jr.: *Sep. Sci. Technol.* **16**, 519 (1981).
4. R. C. Hegelson, J. M. Timko, and D. J. Cram: *J. Am. Chem. Soc.* **95**, 3023 (1973).
5. M. Newcomb and D. J. Cram: *J. Am. Chem. Soc.* **97**, 1257 (1977).
6. H. Nakamura, M. Tagaki, and T. Ueno: *Talanta* **26**, 921 (1979).
7. L. A. Frederick, T. M. Fyles, N. P. Gurprasad, and D. M. Whitfield: *Can. J. Chem.* **59**, 1724 (1981).
8. R. A. Bartsch, G. S. Heo, S. I. Kang, Y. Liu, and J. Strzelbicki: *J. Org. Chem.* **47**, 457 (1982).
9. K. Kimura, I. Maeda, and T. Shono: *Talanta* **26**, 945 (1979).
10. J. J. Christensen, J. D. Lamb, S. R. Izatt, S. E. Starr, G. C. Weed, M. S. Astin, S. D. Stitt, and R. M. Izatt: *J. Am. Chem. Soc.* **100**, 3219 (1978).
11. N. Yamazaki, S. Nakahama, A. Hirao, and S. Negi: *Tetrahedron Letters* **27**, 2429 (1978).

12. J. D. Lamb, J. J. Christensen, J. L. Oscarson, B. L. Nielsen, B. W. Asay, and R. M. Izatt: *J. Am. Chem. Soc.* **102**, 6820 (1980).
13. J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Redke, M. S. Astin, and R. M. Izatt: *J. Am. Chem. Soc.* **102**, 3399 (1980).
14. T. M. Fyles, V. A. Malik-Dimer, and D. M. Whitfield: *Can. J. Chem.* **59** 1734 (1981).
15. J. D. Lamb, R. M. Izatt, D. G. Garrick, J. S. Bradshaw, and J. J. Christensen: *J. Membrane Sci.* **9**, 83 (1981).
16. J. J. Christensen, J. D. Lamb, P. R. Brown, J. L. Oscarson, and R. M. Izatt: *Sep. Sci. Technol.* **16**, 1193 (1981).
17. J. Strzelbicki and R. A. Bartsch: *Anal. Chem.* **53**, 1894 (1981).
18. J. Strzelbicki and R. A. Bartsch: *Anal. Chem.* **53**, 2247 (1981).
19. J. Strzelbicki and R. A. Bartsch: *Anal. Chem.* **53**, 2251 (1981).
20. J. Strzelbicki and R. A. Bartsch: *J. Membrane Sci.* **10**, 35 (1982).
21. J. Strzelbicki, G. S. Heo, and R. A. Bartsch: *Sep. Sci. Technol.* **17**, 635 (1982).
22. W. A. Charewicz and R. A. Bartsch: *J. Membrane Sci* **12**, 323 (1983).
23. W. A. Charewicz and R. A. Bartsch: *Anal. Chem.* **54**, 2300 (1982).
24. W. A. Charewicz and G. S. Heo, and R. A. Bartsch: *Anal. Chem.* **43**, 2094 (1982).
25. J. D. Lamb, R. M. Izatt, P. A. Robertson, and J. J. Christensen: *J. Am. Chem. Soc.* **102**, 2452 (1980).
26. M. P. Biehl, R. M. Izatt, J. D. Lamb, and J. J. Christensen: *Sep. Sci. Technol.* **17**, 289 (1982).
27. R. A. Bartsch, Y. Liu, S. I. Kang, B. son, G. S. Heo, P. G. Hipes, and L. J. Bills: *J. Org. Chem.* **48**, 4864 (1983).
28. A. Martell and L. G. Sillen: *Stability Constants*, Special Publication No. 17, The Chemical Society, Burlington House, London 1964, p. 151.
29. J. D. Lamb, R. M. Izatt, and J. J. Christensen: in *Progress in Macrocyclic Chemistry*, vol. 2, Eds. R. M. Izatt and J. J. Christensen, p. 52, Wiley, New York (1981).
30. R. Hilgenfeld and W. Saenger: in *Host-Guest Complex Chemistry II*, Ed. F. Vögtle, p. 43, Springer-Verlag, New York (1982).
31. C. S. G. Phillips and R. J. P. Williams: *Inorganic Chemistry*, vol. 1, p. 152, Oxford University Press, New York (1965).
32. K. Nakamoto, J. Fujita, M. Kabayashi, and R. Tsuchida: *J. Chem. Phys.* **27**, 439 (1957).
33. A. Rauk, L. C. Allen, and E. Clementi: *J. Chem. Phys.* **52**, 4133 (1970).
34. K. Nakamoto: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, p. 199, Wiley, New York (1978).
35. T. Moeller: *Qualitative Analysis – An Introduction to Equilibrium and Solution Chemistry*, p. 318, McGraw-Hill, New York (1958).
36. H. M. Colquhoun, J. F. Stoddart, and D. J. Williams: *J. Chem. Soc., Chem. Commun.* 847 (1981).
37. H. M. Colquhoun, J. F. Stoddart, and D. J. Williams: *J. Chem. Soc., Chem. Commun.* 849 (1981).
38. H. M. Colquhoun, D. F. Lewis, J. F. Stoddart, and D. J. Williams: *J. Chem. Soc., Dalton Trans.* 607 (1983).
39. H. M. Colquhoun, J. F. Stoddart, and D. J. Williams: *Angew. Chem. Int. Ed.* **25**, 487 (1983).
40. D. R. Alston, J. F. Stoddart, and D. J. Williams: *J. Chem. Soc., Chem. Commun.* 532 (1985).