Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Ion-Pair Extraction of Alkali Mental Nitrate Salts by Lipophilic, Benzo-Substituted 24-Crown-8 Ethers

Richard A. Sachleben[a]; Yanpei Deng[a]; Bruce A. Moyer[a]
[a] Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN

To cite this Article Sachleben, Richard A. , Deng, Yanpei and Moyer, Bruce A.(1997) 'Ion-Pair Extraction of Alkali Mental Nitrate Salts by Lipophilic, Benzo-Substituted 24-Crown-8 Ethers', Separation Science and Technology, 32: 1, 275 — 284
To link to this Article: DOI: 10.1080/01496399708003199
URL: http://dx.doi.org/10.1080/01496399708003199

SEPARATION SCIENCE AND TECHNOLOGY, 32(1-4), pp. 275-284, 1997

ION-PAIR EXTRACTION OF ALKALI METAL NITRATE SALTS BY LIPOPHILIC, BENZO-SUBSTITUTED 24-CROWN-8 ETHERS

Richard A. Sachleben, Yanpei Deng, and Bruce A. Moyer
Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
MS-6119/4500S, PO Box 2008
Oak Ridge, TN 37831-6119

ABSTRACT

The extraction of alkali metal nitrate salts by 24-crown-8 ethers bearing multiple benzo substituents has been surveyed in 1,2-dichloroethane diluent at 25 °C. The results reveal that the addition of benzo-substituents onto the 24-crown-8 increases both the extraction efficiency and the selectivity for the larger cations. Substitution of branched alkyl groups onto the benzo rings of 24-crown-8 ethers has a relatively small influence on their extraction properties.

INTRODUCTION

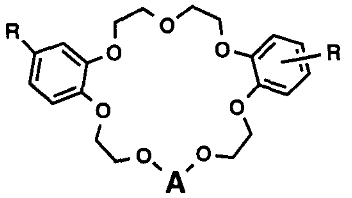
The fission product ^{137}Cs is one of the major radioactive byproducts of nuclear fuel reprocessing (1-3), and the resulting environmental, health, safety, and processing concerns (1,4,5) have led to considerable interest in extractive methods for the separation of Cs^+ from aqueous media (3,6-18). Crown ethers are known to complex alkali and alkaline-earth cations (19-22) and have been intensively studied for the solvent extraction of these metals, including cesium (9-18,23,24). These studies have indicated that the highest cesium selectivity is achieved using benzo-substituted crown ethers of the appropriate size to accommodate the Cs^+ cation, that is, benzo- and dibenzo-21-crown-7 ethers (13,25,26). Surprisingly, the next larger crown ethers, based on 24-crown-8, are less selective for cesium over the smaller cations. (17,20-22). However, the crown ethers used in these studies have been limited to those compounds incorporating two benzo or two cyclohexano substituents (9-11,17,18). Structural studies have shown that the larger crown ethers can "wrap around" the smaller cations (27,28). Undoubtedly, the number and positioning of benzo substitutents will impose constraints on the ability of large crown ethers to act in such a manner. Hence, it was of interest to examine the effect of the number of benzo substituents on extraction strength and selectivity among the alkali metals, as was done previously for 18-crown-6 ethers (29).

For practical application in solvent extraction, crown ethers must exhibit both high solubility in organic diluents and low distribution to the aqueous phase (high lipophilicity) (30). The addition of benzo substituents to crown ethers typically results in an increase in lipophilicity but often reduces their solubility in organic diluents (31). Both solubility and lipophilicity can be increased by alkylation of the benzo substituent (19,32). It is generally accepted that the addition of alkyl substituents to the 4 or 5 position of the benzene ring in benzo-substituted crown ethers has little effect on the extraction properties of these compounds (33,34).

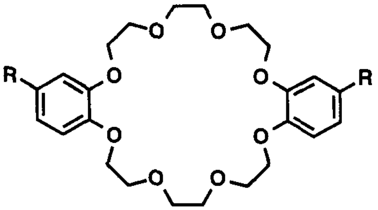
We have been systematically investigating the structural factors that influence efficiency and selectivity in the extraction of alkali metal salts by crown ethers (17,18,35,36). Herein, we report data on the extraction of alkali metal nitrate salts by solutions of crown ethers in 1,2-dichloroethane (DCE) diluent. The crown ethers investigated include benzo-substituted 24-crown-8 ethers bearing two, three, and four aromatic substituents, where the aromatic substituents include benzo, 4-t-butylbenzo, and 4-t-octylbenzo groups (Figure 1). For comparison, corresponding data for similarly substituted 21-crown-7 ethers is presented (17). These results demonstrate the significant influence substituent groups have on both selectivity and efficiency in the extraction of alkali metal salts by these crown ethers.

EXPERIMENTAL

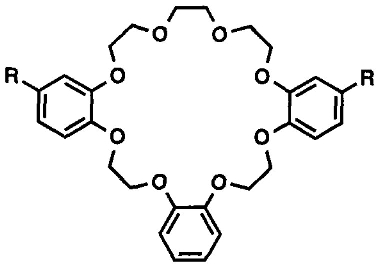
Dibenzo-21-crown-7 (**B_221C7**), bis-t-butylbenzo-21-crown-7 (**bB_221C7**), and dibenzo-24-crown-8 (**B_224C8**) were purchased from Parish Chemical Company and dried under high vacuum without further purification. Tribenzo-24-crown-8 (**B_324C8**) and tetrabenzo-24-crown-8 (**B_424C8**) were prepared using literature methods (19 and 37, respectively). Bis-t-butylbenzo,dibenzo-24-crown-8 (**bB_2B_224C8**) and bis-t-octylbenzo-dibenzo-24-crown-8 (**oB_2B_224C8**) were prepared by the same procedure as **B_424C8**, from t-butylcatechol and t-octylcatechol, respectively. The remaining crown ethers were prepared as described elsewhere (38).



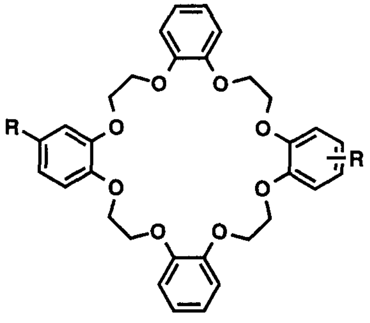
B_221C7: R = H, A = CH_2CH_2
bB_221C7: R = *t*-Butyl, A = CH_2CH_2
oB_221C7: R = *t*-Octyl, A = CH_2CH_2
B_321C7: R = H, A = 



B_224C8: R = H
bB_224C8: R = *t*-Butyl
oB_224C8: R = *t*-Octyl



B_324C8: R = H
bB_2B24C8: R = *t*-Butyl
oB_2B24C8: R = *t*-Octyl



B_424C8: R = H
bB_2B_224C8: R = *t*-Butyl
oB_2B_224C8: R = *t*-Octyl

FIGURE 1. Crown ethers used in this study; *t*-Butyl = $(CH_3)_3C$-, *t*-Octyl = $(CH_3)_3C$-CH_2-$(CH_3)_2C$-.

The extraction experiments were performed in the following manner. Equal volumes (0.5 mL each) of organic phase (0.025 M of crown ether) and aqueous phase (mixture of metal nitrate salts, MNO_3, each at 0.4 M where M = Li^+, Na^+, K^+, Rb^+, and Cs^+) were equilibrated by repeated inversion on a Glascol® laboratory rotator in a thermostated air box at 25.0 °C (± 0.5 °C) for 2 to 15 hours; this procedure was determined previously to be sufficient to ensure equilibrium. The samples were centrifuged for 5 to 10 minutes. An aliquot of the organic phase (0.3 mL) was removed and contacted with 3.0 mL of water, following the same procedure as for the extraction. This back-extraction sample was centrifuged, and 2.0 mL of the aqueous phase was removed for analysis. A second back-extraction showed that essentially all of the metal salts are removed from the solvent in the first back-extraction. The final metal ion concentrations in the organic phase were calculated on the basis of the first stripping results. Multiple (3 - 5) extraction runs were performed for each crown ether solution.

Metal cation analysis of aqueous solutions was performed on a Dionex 2020i ion chromatography system equipped with a autosampler, AI-450 workstation, and conductivity detector, using a Dionex IonPac CS12 cation exchange column with 0.02 m methanesulfonic acid as the eluent. Calculations were based on an average of three injections for each sample using the external standard method. Lower detection limits for Li^+, K^+, Rb^+, and Cs^+ were $[M^+] \geq 3 \times 10^{-6}$; the lower limit for $[Na^+] \geq 10^{-4}$ resulted from the high background of Na^+ in the controls. Acid-treated polypropylene vials and containers were used for both extraction and storage of aqueous solutions. All organic solutions were stored in Teflon® containers.

RESULTS AND DISCUSSION

The extraction of alkali metal nitrate salts by **B_221C7** and **B_224C8** in DCE is shown in Figure 2. These data are consistent with previous studies demonstrating that **B_221C7** extracts rubidium and cesium much more strongly than the smaller alkali metal cations, while the larger macrocycle **B_224C8** exhibits overall weaker extraction and a less pronounced increase in extraction as the size of the cation increases (17). The effect of incorporating three or four benzo substituents into the two macrocyclic systems, 21-crown-7 and 24-crown-8, is shown in Figure 3. The incorporation of three benzo substituents into a 21-crown-7 ether (**B_321C7**) results in a

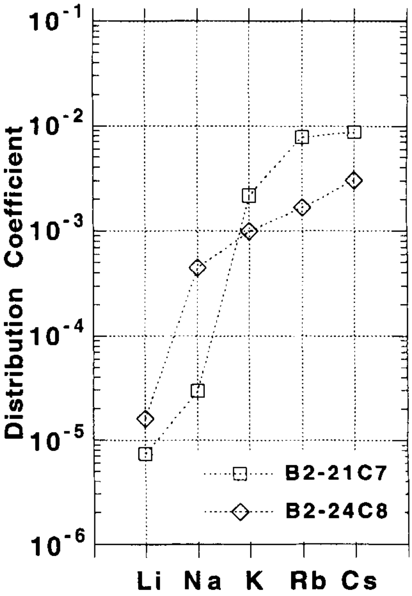


FIGURE 2. Extraction of alkali metal nitrate salts by dibenzo crown ethers.

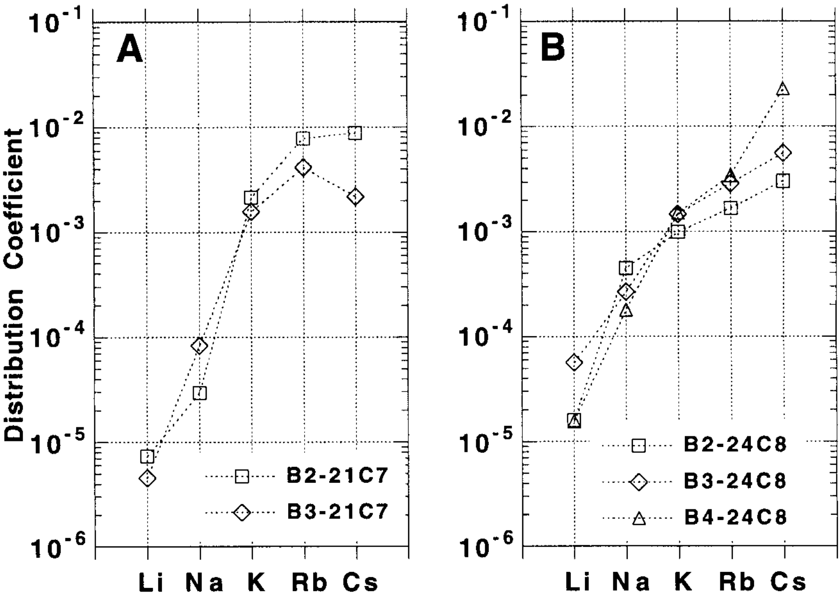


FIGURE 3. Extraction of alkali metal nitrate salts by crown ethers bearing multiple benzo substituents: A) 21-crown-7 ethers, B) 24-crown-8 ethers.

decrease in the extraction of the nitrate salts of the larger alkali metals K, Rb, and Cs. However, this effect is most pronounced for cesium, resulting in selectivity for rubidium extraction (17). Conversely, the addition of one (**$B_3$24C8**) or two (**$B_4$24C8**) benzo substituents to **$B_2$24C8** results in an increase in the extraction of the three larger cations, K^+, Rb^+, and Cs^+. This effect is most pronounced for the extraction of cesium nitrate by **$B_4$24C8**, which extracts cesium nitrate much more strongly than rubidium nitrate and more strongly than any of the other crown ethers in this study.

The effect that alkyl substitution on the benzene ring has on the extraction of alkali metal nitrate salts by the series of 21-crown-7 and 24-crown-8 ethers bearing benzo, *t*-butylbenzo, and *t*-octylbenzo substituents is shown in Figure 4. In general, a relatively small influence is seen in the overall strength of extraction, or in trends with respect to cation size, by the substitution of *t*-butyl or *t*-octyl onto these series of crown ethers. However, subtle systematic differences in the extraction of the different salts can be observed for the dibenzo-21-crown-7 system (*vida infra*).

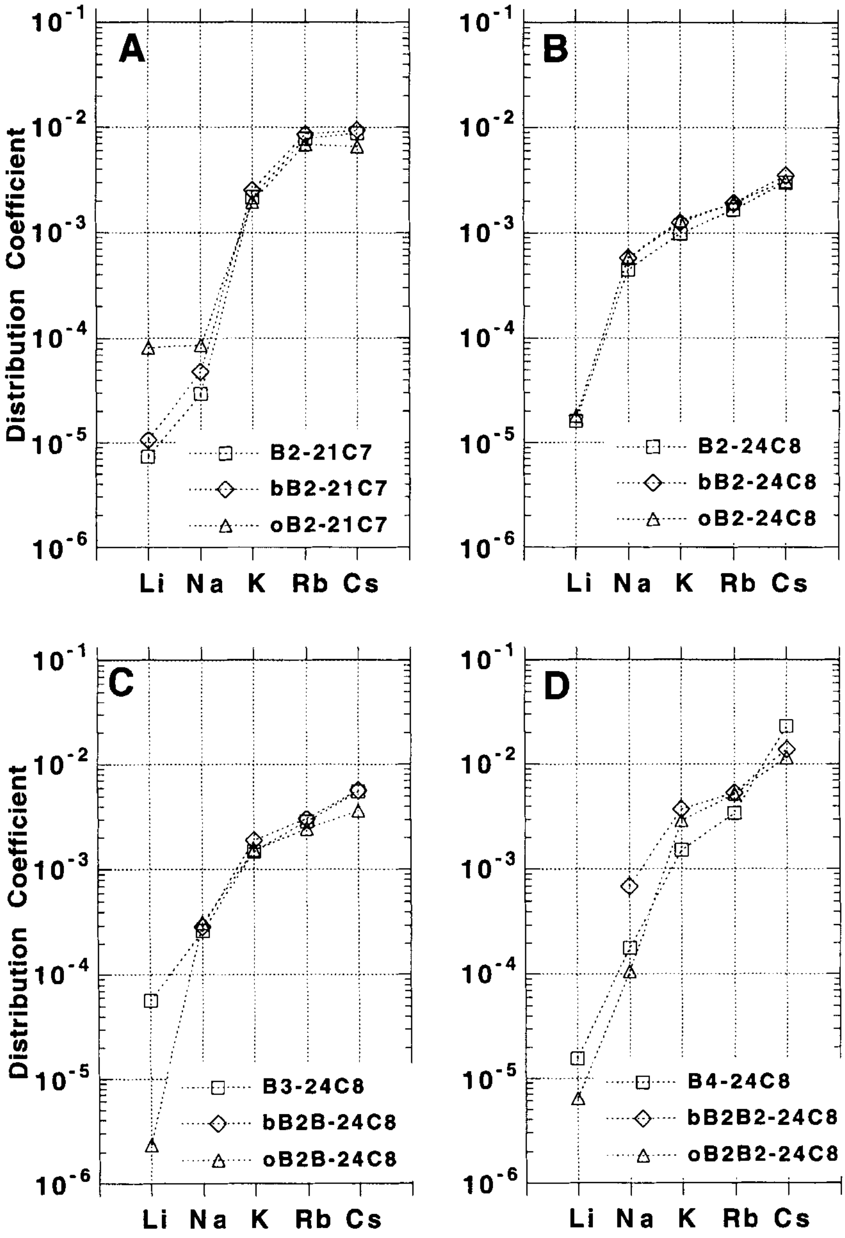


FIGURE 4. Extraction of alkali metal nitrate salts by *t*-alkylbenzo substituted crown ethers.

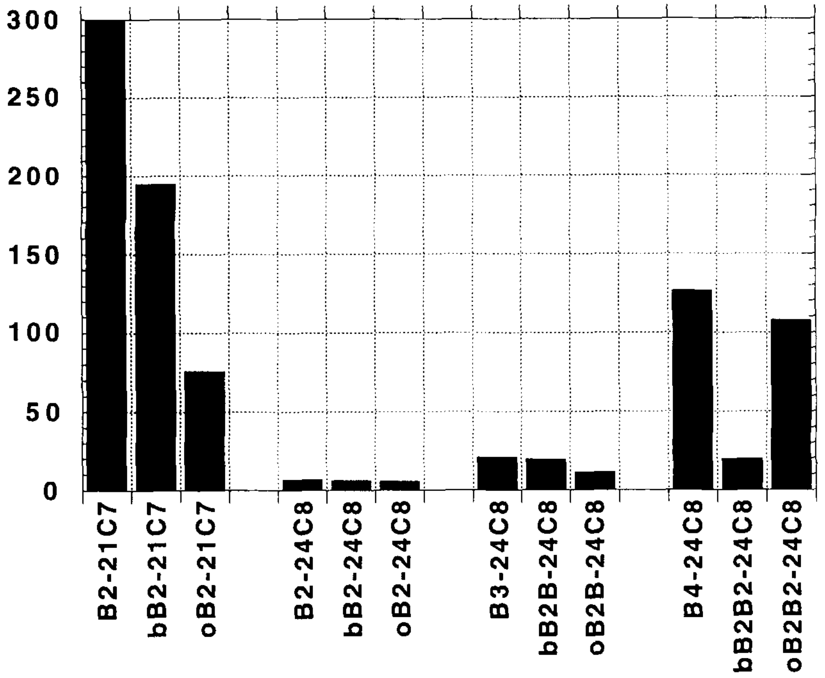


FIGURE 5. Separation factors, $\alpha = D_{Cs} / D_{Na}$, for the crown ethers studied.

For nuclear waste applications, a practical cesium extraction system must exhibit high selectivity for Cs^+ ion relative to Na^+ ion. A histogram of the selectivity for cesium extraction as compared to sodium extraction by this series of crown ethers is shown in Figure 5. The separation factor, $\alpha = D_{Cs} / D_{Na}$, is plotted for each of the crown ethers studied in Figure 4. The effect of adding alkyl substituents to the benzene rings of the 24-crown-8 ethers is relatively minor, in contrast to the effect in the dibenzo-21-crown-7 series. In previous reports (17,18,35), we have noted an increase in the extraction of sodium when **B$_2$21C7** is substituted with *t*-alkyl groups (see Fig. 4a). This change in the distribution coefficient for sodium extraction results in a significant decrease in cesium/sodium selectivity for the dibenzo-21-crown-7 system (i.e. from **B$_2$21C7** to **oB$_2$21C7**). A similar but significantly smaller trend is observed in the 24-crown-8 systems. Consequently, while **B$_2$21C7** exhibits the highest cesium selectivity overall, **oB$_2$B$_2$24C8** exhibits the best cesium selectivity among the *t*-octylbenzo-substituted crown ethers, exceeding that of **oB$_2$21C7**.

CONCLUSION

A survey of the extraction of alkali metal nitrate salts by benzo and *t*-alkylbenzo substituted crown ethers has revealed that incorporation of multiple aromatic substituents into 21-crown-7 and 24-crown-8 ethers can have profound effects on the properties of these extractants. Whereas varying the number of aromatic substituents significantly affects both the extraction strength and the extraction selectivity of these compounds, varying the substituents on the benzene rings has a relatively small effect on the extraction strength. However, even small changes in extraction strength can result in significant differences in selectivity, especially for the dibenzo-21-crown-7 series, where alkyl substituents significantly reduce the selectivity for cesium ($\alpha_{Cs/Na}$) extraction. Conversely, addition of *t*-alkyl groups to benzo-substituted 24-crown-8 ethers has little effect on either extraction strength or selectivity. Thus, the tetrabenzo-24-crown-8 system shows promise for the efficient, selective extraction of cesium from mixtures of alkali metal salts.

ACKNOWLEDGEMENTS

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-840R21400 with Lockheed Martin Energy Systems, Inc. We would like to thank Drs. Richard Carter and Donald Palmer for assistance in the ion chromatographic analyses.

REFERENCES

(1) L. Cecille, *Radioactive Waste Management and Disposal*, Elsevier: London (1991).

(2) W. W. Schulz and L. A. Bray, Sep. Sci. Techol., *22*, 191 (1987).

(3) E. Blasius and K.-H. Nilles, Radiochimica Acta, *35*, 173 (1984).

(4) *Basic Research for Environmental Research,* Vol. DOE/ER-0482T, U.S. Department of Energy, O. E. R., U.S. Government Printing Office, Washington, D.C., 1990.

(5) E. P. Horwitz and W. W. Schulz, *Basic Research Needs for Management and Disposal of DOE Wastes*, Vol. DOE/ER-0492T, U.S. Government Printing Office, Washington, D.C., 1991.

(6) L. Cecille, M. Casarci, and L. Pietrelli, Eds., *New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications*, Elsevier, Amsterdam, 1991.

(7) E. A. Filippov, A. K. Dzekun, I. V. Mamakin, V. M. Gelis, and V. V. Miyutin, in *Waste Management,* R. G. Post and M. E. Wacks, Eds., Arizona Board of Regents, Tucson, Arizona, 1992, p. 1021.

(8) *Feasibility of Separation and Utilization of Caesium and Strontium from High Level Liquid Waste*, Technical Reports Series No. 356, IAEA, Vienna, 1993.

(9) I. H. Gerow and M.W. Davis, Jr., Sep. Sci. Technol., *14*, 395 (1979).

(10) I. H. Gerow, *The Use of Macrocyclic Ethers to Remove Cesium-137 from Acidic Nuclear Wastes by Solvent Extraction*, PhD Dissertation, University of South Carolina, 1980.

(11) I. H. Gerow, J. E. Smith Jr., and M.W. Davis, Jr., Sep. Sci. Technol., *16*, 519 (1981).

(12) K.-H. Nilles, PhD Dissertation, Universitat des Saarlandes, Saarbrucken, 1978.

(13) W. J. McDowell, G. N. Case, J. A. McDonough, and R. A. Bartsch, Anal. Chem., *64*, 3013 (1992).

(14) R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.-F. Dozol, C. Hill, and H. Rouquette, Angew. Chem, Int. Ed. Engl., *33*, 1506 (1994).

(15) A. Casnati, A. Pocjini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. de Jong, and D. N. J. Reinhoudt, J. Chem. Am. Soc., *117*, 2767 (1995).

(16) J.-F. Dozol, J. Casas, and A. M. Sastre, Sep. Sci. Technol., *30*, 435 (1995).

(17) Y. Deng, R. A. Sachleben, and B. A. Moyer, Solvent Extr. Ion. Exch., in press.

(18) Y. Deng, R. A. Sachleben, and B. A. Moyer, Proceedings of ISEC'96, in press.

(19) C. J. Pedersen, J. Am. Chem. Soc., *89*, 2495 (1967).

(20) J. J. Christensen, D. J. Eatough, and R. M. Izatt, Chem. Rev., *74*, 351 (1974).

(21) R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, and D. Sen, Chem. Rev., *85*, 271 (1985).

(22) R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R. L. Bruening, Chem. Rev., *91*, 1721 (1991).

(23) R. A. Schwind, T. J. Gilligan, and E. L. Cussler, in *Synthetic Multidentate Macrocyclic Compounds*, R. M. Izatt and J. J. Christensen, Eds., Academic Press: New York, 1978, p 289, and references cited therein.

(24) W. J. McDowell, Sep. Sci. Technol., *23*, 1251 (1988), and references cited therein.

(25) J.-F. Dozol, J. Casas, and A. M. Sastre, in *New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications*, L. Cecille, M. Casarci, and L. Pietrelli, Eds., Elsevier, Amsterdam, 1991, p. 163.

(26) J.-F. Dozol, in *New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications*, L. Cecille, M. Casarci, and L. Pietrelli, Eds., Elsevier, Amsterdam, 1991, p. 173.

(27) N. K. Dalley, in *Synthetic Multidentate Macrocyclic Compounds*, R. M. Izatt and J. J. Christensen, Eds., Academic Press: New York, 1978, p. 207.

(28) J. D. Owen, Acta. Crystallogr., Sect. C., *39*, 861 (1983).

(29) O. Heitzsch, K. Gloe, A. Sabela, J. Koryta, and E. Weber, J. Incl. Phenom., *13*, 311 (1992).

(30) B. Cox, and H. Schneider, *Coordination and Transport Properties of Macrocyclic Compounds in Solution*, Elsevier, Amsterdam (1992).

(31) C. J. Pedersen, in *Synthetic Multidentate Macrocyclic Compounds*, R. M. Izatt and J. J. Christensen, Eds., Academic Press, New York, 1978, p. 1.

(32) L. Tusek, P. R. Danesi, and R. J. Chiarizia, Inorg. Nucl. Chem., *37*, 1538 (1975).

(33) C. S. Chen, S. J. Wang, and S. C. Wu, Inorg. Chem., *23*, 3901 (1984).

(34) T. B. Stolwijk, E. J. R. Sudölter, and D. N. Reinhoudt, J. Am. Chem. Soc., *111*, 6321 (1989).

(35) Y. Deng, R. A. Sachleben, and B. A. Moyer, J. Chem. Soc., Faraday Trans., *23*, 4215 (1995).

(36) R. A. Sachleben, M. C. Davis, J. J. Bruce, E. S. Ripple, J. L. Driver and B. A. Moyer, Tetrahedron Letters, *34* (34), 5373 (1993).

(37) G. R. Brown and A. J. Foubister, J. Med. Chem., *26*, 590 (1983).

(38) R. A. Sachleben, J. M. Lavis, J. H. Burns, and J. C. Bryan, Tetrahedron, submitted.