

09.4-12 f-ELEMENT/CROWN ETHER COMPLEXES. STRUCTURAL EFFECTS OF SOLVENT AND WATER OF HYDRATION HYDROGEN BONDING. By Robin D. Rogers, Department of Chemistry, Northern Illinois University, DeKalb, IL 60115 U.S.A.

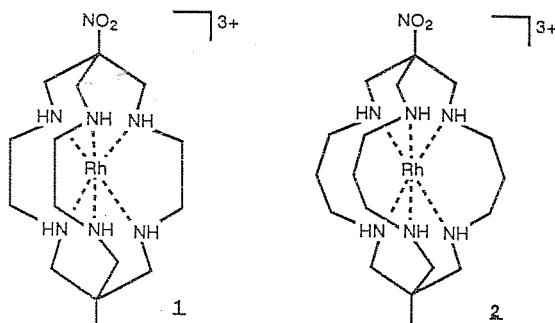
Much of our current research in f-element/crown ether chemistry has focused on the synthesis and structural characterization of crown ether complexes with hydrated f-element salts (and Y³⁺) in order to investigate the effects of metal size, crown ether cavity size and conformation, anion, solvent polarity, and reaction and crystallization conditions on overall structure and bonding in these complexes. During the course of this work we have characterized several complexes with intricate networks of hydrogen bonding resulting from the interaction of metal coordinated water or solvent molecules, anions, and crown ether molecules. This paper will survey our results in this area and attempt to show how hydrogen bonding patterns influence overall structure, crown conformation, and metal ion geometry. The structures of the following complexes from our group will be discussed: [Tb(OH₂)₂(12-crown-4)]Cl₂·2H₂O, [Lu(OH₂)₄][Na(12-crown-4)]₂Cl₄·2H₂O, [Lu(OH₂)₂Cl]₂·1.5(12-crown-4)·2H₂O, [M(OH₂)₂Cl]₂·15-crown-5 (M = Y, Gd, Lu), [Y(NO₂)₂(OH₂)₂][NO₂]₂(15-crown-5), [(OH₂)₂(15-crown-5)]₂·[UO₂Cl₄]₂·2CH₃CN, [UO₂(OH₂)₂][ClO₄]₂·3(15-crown-5)·CH₃CN, [Y(NO₂)₂(OH₂)₂][X]·benzo-15-crown-5·0.5CHMe (X = CH₃CN or OHMe), [MCl(OH₂)₂(18-crown-6)]Cl₂·2H₂O (M = Sm, Gd, Tb), [M(OH₂)₂(OHMe)][MCl(OH₂)₂(18-crown-6)]₂·Cl₂·2H₂O (M = Y, Dy), [Dy(OH₂)₂Cl]₂·18-crown-6·4H₂O, [UO₂(OH₂)₂][ClO₄]₂·2(18-crown-6)·2CH₃CN·H₂O, ThCl₄·(OH₂)₂·18-crown-6·H₂O, Th(NO₂)₄(OH₂)₂·18-crown-6, and [(OH₂)₂(dibenzo-18-crown-6)]₂·[UO₂Cl₄]₂·2CH₃CN. Other results will be included as they become available.

09.4-13 f-ELEMENT/CROWN ETHER COMPLEXES. CROWN CONFORMATIONS IN HYDROGEN BONDED COMPLEXES OF HYDRATED ACTINIDE SALTS. Matthew M. Benning and Robin D. Rogers, Department of Chemistry, Northern Illinois University, DeKalb, IL 60115 U.S.A.

In working towards a better understanding of f-element/ ionophore complexation, we are investigating reactions between hydrated actinide salts and crown ethers. In the compounds we have structurally studied: [(OH₂)₂(15-crown-5)]₂·[UO₂Cl₄]₂·2CH₃CN, [(OH₂)₂(dibenzo-18-crown-6)]₂·[UO₂Cl₄]₂·2CH₃CN, [UO₂(OH₂)₂][ClO₄]₂·3(15-crown-5)·CH₃CN, [UO₂(OH₂)₂][ClO₄]₂·2(18-crown-6)·2CH₃CN·H₂O, and [Th(NO₂)₄(OH₂)₂]₂(18-crown-6), the crown ether oxygen atoms are hydrogen bonded to the water molecules coordinated to the metal. [ThCl₄(OH₂)₂(OH₂)₂]₂(18-crown-6)·H₂O contains the crown ether hydrogen bonded to not only a water molecule but also solvent molecules coordinated to the metal. This paper will examine the number of crown oxygen atoms involved in the hydrogen bonding and the extent to which these interactions effect the conformation of the crown ether. The above structures as well as other current work will be discussed.

09.4-14 [Rh(MENOsar)]ZnCl₄·Cl₂·3H₂O AND [Rh(MENOTar)]ZnCl₄·Cl₂·3H₂O: THE EFFECT OF THE SIZE OF THE CAVITY OF THE ENCAPSULATING LIGAND ON THE METAL-NITROGEN BOND LENGTHS. By R.J. Geue, M.B. McDonnell, A.M. Sargeson and A.C. Willis, Research School of Chemistry, Australian National University, Canberra, A.C.T., Australia.

The structures of the two closely related Rh³⁺ metal-cage species, [Rh(MENOsar)]ZnCl₄·Cl₂·3H₂O, 1, and [Rh(MENOTar)]ZnCl₄·Cl₂·3H₂O, 2,



were undertaken to aid the interpretation of electrochemical results.

Crystal data for 1: P2₁/c, a = 11.088(1), b = 9.878(1), c = 25.654(2)Å, β = 93.13(1)°; and for 2: P2₁/c, a = 11.190(1), b = 10.114(1), c = 26.702(3)Å, β = 90.87(1)°. Data were collected on a Picker FACS-I diffractometer using Cu Kα radiation yielding 4560 observed reflections for 1 and 4440 for 2. Final R factors were 0.043 and 0.044 respectively.

The trimethylene linkages in 2 give rise to a larger cavity at the centre of the ligand and force the Rh-N distances (2.102(3)-2.117(3)Å) to be significantly longer than in 1 (2.056(3)-2.077(3)Å). The twist angle about the approximate 3-fold axis changes from 52° for 1 to 66° for 2.