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Complexation of Manganese(II) by Cyclohexano-15-crown-5 in Propylene Carbonate: Calorimetric and X-ray Crystallographic Investigation[†]

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Calorimetric titrimetry reveals that cyclohexano-15-crown-5 (C15C5) forms a 1:1 complex with Mn(II) ions (2.5 mM) in propylene carbonate (PC) solution to which was added levels of water up to 134 mM. The reaction proceeds with a strong driving force (log $K = 4.7-5.0$) and is enthalpically driven overall, but the magnitude of the enthalpy change decreases with increasing water concentration in the case of the Mn(II) nitrate salt. A minor anion effect occurs in which the trifluoromethansulfonate ion gives slightly more negative values of ΔH and $T\Delta S$ than the nitrate ion. Values of log K, however, do not change appreciably with increasing water concentration, nor are they dependent on the anion. The crystal structure of Mn(C15C5)(CF$_3$SO$_3$)$_2$ was determined, showing that the Mn(II) ion is coordinated by a pentagonal bipyramid of oxygen atoms provided by the equatorial crown ether and apical monodentate triflate ions. Crystal data for MnC$_{16}$H$_{26}$O$_{11}$F$_6$S$_2$: monoclinic, $C2/c$, $a = 26.925(3)$ Å, $b = 14.145(1)$ Å, $c = 13.420(1)$ Å, $\beta = 100.31(2)°$, $V = 5028$ Å^3, $Z = 8$, $t = 26$ °C. For 2178 reflections with $I > \sigma(I)$, and 325 parameters, $R(F) = 0.050$ and $R_w(F) = 0.054$.

Introduction

Crown ethers have been studied predominantly in the context of their remarkable ability to selectively complex alkali and alkaline earth metal ions. By reference to the concept of hard and soft acids and bases,[1] the borderline and soft transition metal ions may be considered unsuitable guests for crown ethers, which have hard ether-type oxygen donor atoms. Indeed, binding constants for the divalent first-row transition metal ions tend to be relatively low.[2] In one notable case, complexation of Mn(II) by 12-crown-4, 15-crown-5, or 18-crown-6 in water could not be detected by ESR.[3] Accordingly, successful attempts to measure the thermodynamic binding constants of first-row transition metal ions by crown ethers have employed nonaqueous solvents, where the competing solvation of the free cation is diminished.[4−6] Structural studies reveal that under relatively dry conditions inner-sphere coordination of the divalent metals Mn(II)−Zn(II) may be achieved by crown ethers,[7,8] and the size-matched 15-crown-5 (15C5) ether and its derivatives generally form pentagonal bipyramidal complexes involving intracavital binding of the metal cation by the five ether oxygen atoms.[9] From the structural evidence, the anion, solvent, and water also participate to varying degrees in the coordination of the metal cations. Under sufficiently wet crystallization conditions, transition metal compounds with crown ethers often involve extensive hydration of the metal ion where the crown ether is relegated to a hydrogen-bonding role in the secondary coordination sphere.[10]

An especially noteworthy feature of the coordination of the divalent first-row transition metals Mn(II)−Zn(II) by the particular crown ethers benzo-15-crown-5 (B15C5), cyclohex-

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ano-15-crown-5 (C15C5), and *tert*-butylcyclohexano-15-crown-5 (*t*-BC15C5) lies in the unusual selectivity for Mn(II) and Zn(II) essentially according to an inverted Irving–Williams order. This selectivity behavior was first observed in solvent-extraction systems[11,12] and recently in spectrophotometric[6] and calorimetric studies[13] of complexation in nonaqueous solvents. The apparent discrimination against complexation of metal ions having nonspherically symmetric ground states suggests unusual bonding effects. A ligand-field rationale has been advanced.[11,12]

As a logical step toward understanding the fundamental factors determining the Mn(II) selectivity in these systems, we have begun to examine some of the thermodynamic and structural aspects of Mn(II) complexation by C15C5.[8,11–14] In this paper, we present the results of a calorimetric investigation of the complexation of C15C5 with the Mn(II) ion having either nitrate or trifluoromethanesulfonate (triflate) as the counteranion in propylene carbonate (PC), a high-dielectric solvent conferring sufficiently high equilibrium constants, heats, and solubilities for experimental purposes. It was specifically the aim here to determine stoichiometry and thermodynamic parameters and, in addition, to probe the effects of anion type and water concentration. Since water in nonaqueous solvents cannot be avoided entirely and is inherent in solvent extraction, our approach has been to characterize its effect deliberately. To further assist in the interpretation of results, an X-ray crystal structure of the Mn(II) C15C5 triflate complex is reported.

Experimental Section

Materials. Cyclohexano-15-crown-5 (Parish Chemical) was distilled under vacuum at 1.3 Pa and stored in a glovebox maintained at a water concentration below 0.7 ppm. Propylene carbonate (anhydrous, water < 0.005%, Aldrich Chemical) was distilled under reduced pressure and stored over activated 13X molecular sieves (Linde) in the glovebox as required for experiments under dry conditions. The purities of C15C5 and PC were checked by GC and were found to be a key criterion for reproducibility in the experiments. We observed that unpurified C15C5 and PC produced falsely smooth end points in thermograms, resulting in low log *K* values, and the end points were often shifted as well. The manganese(II) nitrate hexahydrate (Aldrich Chemical) was used as received.

Manganese(II) trifluoromethanesulfonate, $Mn(CF_3SO_3)_2$, was prepared according to two procedures: (1) A 14.4-g (0.096-mol) sample of trifluoromethanesulfonic acid (triflic acid, Eastman Kodak) was slowly added to 50 mL of an aqueous suspension of 5.0 g (0.043 mol) of manganese(II) carbonate (Strem Chemical) with stirring. (2) A 60-mL aqueous solution containing 10 g (0.067 mol) of triflic acid (Aldrich Chemical) was slowly added to 1.5 g (0.026 mol) of manganese metal power (Fisher Scientific). In both procedures, a white product was collected by filtration, dried at 50 °C under vacuum at least 12 h, and then recrystallized from mixtures of ether/acetonitrile or ethanol/toluene. (Cyclohexano-15-crown-5)manganese(II) triflate, $Mn^{II}(C15C5)(CF_3SO_3)_2$, was prepared by mixing 0.09 g (0.25 mmol) of $Mn(CF_3SO_3)_2$ and 0.14 g (0.51 mmol) of C15C5 in 25 mL of PC under stirring for at least 12 h at room temperature. The solvent was slowly removed by evaporation under vacuum to yield colorless crystals, which were covered by mineral oil for X-ray crystallography.

Calorimetric Procedures. Procedures, calibrations, and data analyses, including determinations of log *K* and ΔH values by regression methods, were adopted from earlier recommendations.[15] Calorimetric titrations were conducted in the isoperibol mode using a Tronac 450 calorimeter equipped with a personal computer for instrument control, data collection, and data manipulation. Solutions of C15C5 in dry PC were in all cases titrated continuously into Mn(II) solutions, reaching a maximum ligand:metal ratio of 2. All salt solutions were standardized using either EDTA titration or cation exchange followed by acid–base titration. Both the reaction vessel and the buret were thermostated at 25.000 ± 0.001 °C in a water bath. The thermistor was calibrated between 24.5 and 25.5 °C against a precalibrated platinum resistance thermometer. In a typical experiment, a total of 200 points were collected at 5 s intervals; 30 points each were collected for the leading and trail periods, and 140 points were collected for the titration period. The experimental data were collected using a modified commercial program, LabWindows,[16] and manipulated using the programs HEAT, DILCOR, DLKDDH,[17] and SXLSQA.[18] By use of a Brinkmann 652 KF coulometer, the water concentration in the PC solution was measured by Karl Fischer titration immediately after each calorimetric titration. The Karl Fischer reagents were purchased from both Riedel-de Haën Laboratory Chemical and Photovolt and used as received. Water standards for Karl Fischer titration were purchased from Photovolt.

Table 1. Crystallographic Data for (Cyclohexano-15-crown-5)manganese(II) Triflate

formula	$MnC_{16}H_{26}O_{11}F_6S_2$
fw	627.44
space group	*C*2/*c*, No. 15
a, Å	26.925(3)
b, Å	14.145(1)
c, Å	13.420(1)
β, deg	100.31(2)
V, Å^3	5028
Z	8
λ(Mo Kα), Å (graphite monochromator)	0.710 69
d_{obsd}, g cm^{-3}	1.6
d_{calcd}, g cm^{-3}	1.657
t, °C	26
crystal dimens, mm^3	0.64 × 0.32 × 0.36
μ, cm^{-1}	7.6
rel transm	0.95–1.0
2θ range, deg	<46
octants measd	$+h,+k,\pm l$
no. of reflns measd	3500
no. of unique reflns with $I > \sigma(I)$	2178
R_{int}	0.03
no. of params	325
$R(F) = (\sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$	0.052
$R_w(F) = [(\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.054
σ_1	1.47

X-ray Diffraction and Crystal Structure. A prismatic, moisture-sensitive specimen of $Mn^{II}(C15C5)(CF_3SO_3)_2$ was manipulated under oil and sealed in glass for the X-ray study. Data were obtained by use of an Enraf-Nonius CAD-4 diffractometer. Unit-cell dimensions were refined by use of the settings of 25 reflections at 18–22° 2θ. Intensities were measured by $\omega-2\theta$ scans and corrected for Lorentz and polarization effects. Empirical absorption corrections were based on ψ scans, but no correction was made for extinction. Operational details and crystal data are given in Table 1. The calculations were carried out using the structure determination package of Frenz.[19] Multan-82 and Fourier syntheses were used to determine non-hydrogen atomic positions, and hydrogen atoms were added in calculated sites and given isotropic thermal parameters. Least-squares refinement of the quantity $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ was used to adjust the positions and anisotropic thermal

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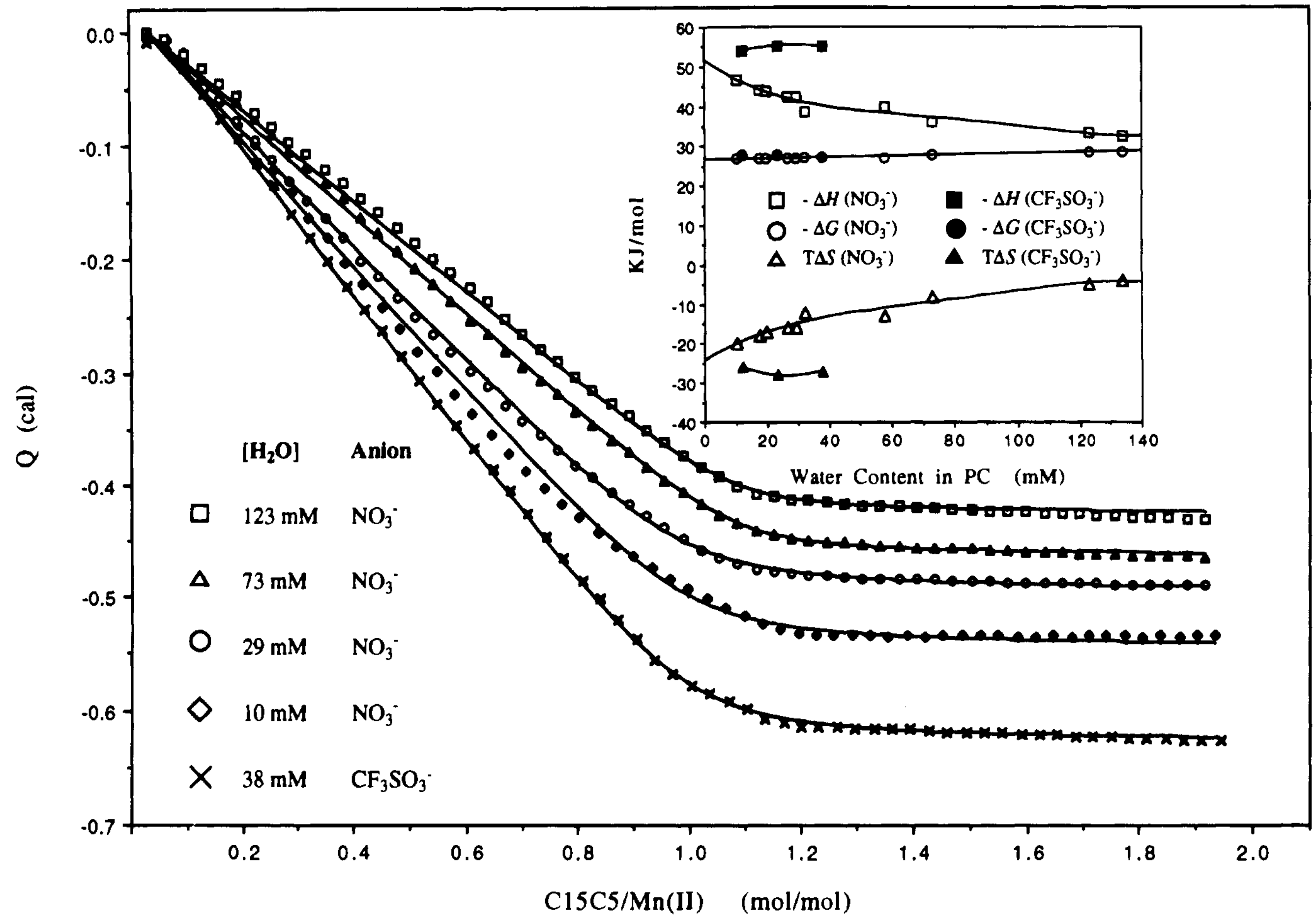


Figure 1. Thermograms of calorimetric titrations of Mn(II) nitrate or triflate salts by C15C5 in propylene carbonate solution at 25 °C for various water concentrations. The symbols represent the experimental data, and the solid lines are the calculated curves. The insert shows plots of the variation of the obtained apparent values of $-\Delta H$, $-\Delta G$, and $T\Delta S$ vs water content.

parameters of all non-hydrogen atoms. Additional details are given in the supplementary material.

Results

Calorimetry. As shown in Figure 1, observed thermograms obeyed 1:1 ligand:metal reaction stoichiometries with identifiable end points. Table 2 lists the determined values of log K and the corresponding thermodynamic parameters for both nitrate and triflate Mn(II) salts in the presence of various concentrations of water. The ΔH values were well determined from the experiments, but the log K values lie close to the experimental limit of the technique[15] and may only be considered precise to approximately ±0.1. Consistent with the behavior of other examples of metal ion binding by crown ethers in nonaqueous media,[2] our results demonstrate an enthalpic driving force compensated partially by an entropy loss in the binding of Mn(II) by C15C5 in wet PC. Complexation of Co^{2+} and Cu^{2+} ions by C15C5 and other crown ethers in PC was also found to be enthalpically driven.[5] Except for the values obtained by extrapolation to zero water concentration, the listed parameters must be taken as apparent values in that they correspond to varying degrees of hydration of reactant and product species.

A minor anion effect may be observed, but apparently only in the presence of water, where triflate ion gives slightly more negative values of ΔH and $T\Delta S$ than nitrate ion. Values of log K, however, appear nearly independent of anion. Increasing water content in the case of the nitrate salt of Mn(II) causes a clear decrease in the magnitude of the ΔH term with essentially constant log K. In the limited range of water concentrations studied, no change in thermodynamic parameters was observed for the triflate salt. Extrapolation to $[H_2O] = 0$ in the case of the nitrate salt gives log $K = 4.6$, $\Delta H = -52$ kJ/mol, and $T\Delta S = -24$ kJ/mol. The values are not appreciably different from

Table 2. Apparent Values of log K, ΔH, and $T\Delta S$ for the 1:1 Ligand:Metal Complexation Reactions of C15C5 with $Mn(NO_3)_2$ and $Mn(CF_3SO_3)_2$ in Propylene Carbonate Solution with Varied Water Contents[a]

reactant	$[H_2O]$, mM	log K	ΔH, kJ/mol	$T\Delta S$, kJ/mol
$Mn(NO_3)_2$	0	4.7[b]	−52[b]	−25[b]
	10.2	4.7	−46.8	−20
	17.2	4.7	−44.2	−18
	19.4	4.7	−43.8	−17
	26.4	4.7	−43.0	−16
	29.2	4.7	−42.5	−16
	32.1	4.8	−38.8	−12
	58	4.7	−40.0	−13
	73	4.9	−36.1	−8
	123	5.0	−33.3	−5
	134	5.0	−32.3	−4
$Mn(CF_3SO_3)_2$	11.9	4.9	−55.7	−28
	23.1	4.9	−54.0	−26
	38.1	4.8	−55.2	−28
	11.9−38.1	4.8[c]	−55.0[c]	−27[c]

[a] At 25.000 ± 0.001 °C with initial Mn(II) concentration = 2.5 mM, ionic strength = 0.0075. Parameter standard errors of fitting lay in the ranges 0.03−0.08 for log K and 0.03−0.09 for ΔH. Values of log K and ΔH were determined directly from the regression analyses of the data; values of $T\Delta S$ were then derived from the relations $\Delta G = -5.71$ log K and $\Delta G = \Delta H - T\Delta S$. [b] Extrapolated to $[H_2O] = 0$ (Figure 1). [c] Average value.

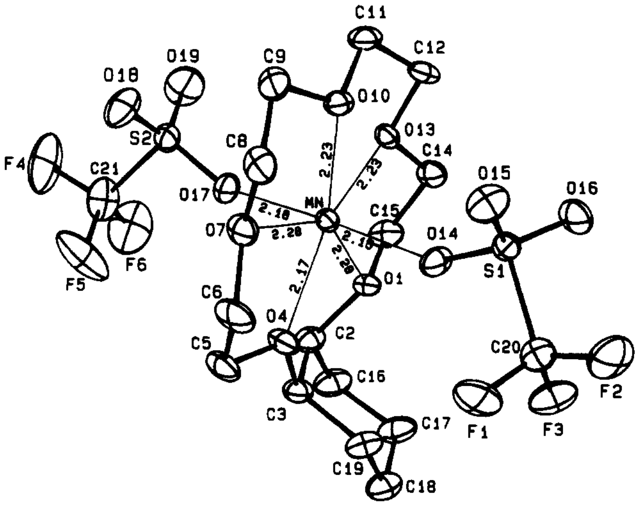


Figure 2. Structure of $Mn(C15C5)(CF_3SO_3)_2$. Atoms are represented as 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters with Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Mn	0.13517(3)	0.82445(5)	0.14304(6)	2.97(2)
S1	0.02299(5)	0.8341(1)	−0.0273(1)	3.59(3)
S2	0.25195(5)	0.8908(1)	0.2786(1)	5.02(4)
F1	0.02804(2)	0.6758(3)	−0.1220(3)	9.3(1)
F2	−0.0425(2)	0.7416(3)	−0.1555(3)	9.3(1)
F3	−0.0191(1)	0.6705(3)	−0.0140(3)	8.4(1)
F4	0.3392(2)	0.8329(4)	0.3715(4)	13.7(2)
F5	0.2965(2)	0.7307(4)	0.2729(4)	14.2(2)
F6	0.2798(2)	0.7614(4)	0.4144(3)	13.1(2)
O1	0.1066(1)	0.7413(2)	0.2666(2)	3.58(8)
O4	0.1510(1)	0.6759(2)	0.1240(3)	4.50(9)
O7	0.1803(1)	0.8102(3)	0.0155(3)	4.70(9)
O10	0.1361(1)	0.9648(2)	0.0681(2)	4.00(9)
O13	0.1070(1)	0.9311(2)	0.2420(2)	3.66(8)
O14	0.0629(1)	0.8005(3)	0.0487(3)	5.2(1)
O15	0.0388(2)	0.8828(3)	−0.1092(3)	6.0(1)
O16	−0.0173(1)	0.8756(3)	0.0108(3)	5.9(1)
O17	0.2067(1)	0.8401(3)	0.2468(3)	5.7(1)
O18	0.2765(2)	0.9222(3)	0.1977(3)	7.7(1)
O19	0.2511(2)	0.9563(4)	0.3561(4)	12.0(2)
C2	0.1402(2)	0.6598(4)	0.2944(4)	4.7(1)
C3	0.1402(2)	0.6081(4)	0.1975(4)	4.4(1)
C5	0.1828(2)	0.6485(4)	0.0566(4)	5.5(2)
C6	0.1755(2)	0.7182(5)	−0.0269(4)	6.4(2)
C8	0.1715(2)	0.8876(4)	−0.0548(4)	5.4(1)
C9	0.1730(2)	0.9766(4)	0.0053(4)	5.4(1)
C11	0.1275(2)	1.0445(4)	0.1287(4)	4.8(2)
C12	0.0884(2)	1.0152(4)	0.1888(4)	4.5(1)
C14	0.0740(2)	0.8900(4)	0.3030(4)	4.9(1)
C15	0.0997(2)	0.8025(4)	0.3490(4)	5.5(2)
C16	0.1226(3)	0.5959(4)	0.3754(5)	6.5(2)
C17	0.0723(2)	0.5516(5)	0.3326(5)	6.7(2)
C18	0.0753(2)	0.4949(5)	0.2375(5)	7.1(2)
C19	0.0918(2)	0.5587(4)	0.1582(5)	5.9(2)
C20	−0.0039(2)	0.7254(5)	−0.0832(5)	5.6(2)
C21	0.2941(2)	0.7992(6)	0.3383(5)	7.3(2)

[a] Isotropic equivalent displacement parameter is defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

the average values found for the triflate salt: $\log K = 4.8$, $\Delta H = -55$ kJ/mol, and $T\Delta S = -27$ kJ/mol.

Crystal Structure. The complex $Mn(C15C5)(CF_3SO_3)_2$ crystallized from PC solution, and its structure is illustrated in Figure 2. Non-hydrogen atomic positions are listed in Table 3, and relevant bond lengths and angles are given in Table 4; additional structural details may be found in the supplementary material. It is seen that the Mn(II) ion is coordinated by a pentagonal bipyramid of oxygen atoms and lies at 0.024(1) Å from the best plane through its equator. These equatorial atoms belong to the crown ether, and apical oxygen atoms are provided by monodentate triflate ions. The cyclohexyl group adopts the expected chair conformation. No solvent or water molecules are present, and the crystal structure consists of discrete complexes held together by nonbonding interactions. Essentially no difference in conformation of the crown ether may be noted in comparison with its conformation in the related complex $[Mn(C15C5)(DtBNS)(H_2O)](DtBNS)\cdot C_7H_8$ (DtBNS is 3,7-di-*tert*-butylnaphthalene-1-sulfonate and C_7H_8 is toluene),[8] where a water molecule and a monodentate sulfonate anion occupy the axial sites.

Table 4. Selected Bond Lengths (Å) and Angles (deg)

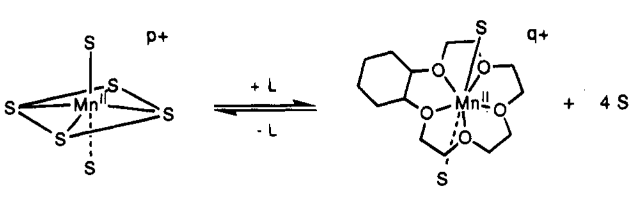
	Bond Lengths		
Mn−O1	2.276(3)	O1−C2	1.472(6)
Mn−O4	2.168(3)	O1−C15	1.442(7)
Mn−O7	2.278(4)	O4−C3	1.442(7)
Mn−O10	2.228(3)	O4−C5	1.406(7)
Mn−O13	2.231(3)	O7−C6	1.418(7)
Mn−O14	2.149(3)	O7−C8	1.437(7)
Mn−O17	2.175(3)	O10−C9	1.422(7)
S1−O14	1.425(4)	O10−C11	1.433(7)
S1−O15	1.425(4)	O13−C12	1.430(6)
S1−O16	1.409(4)	O13−C14	1.434(7)
S1−C20	1.804(6)	C2−C3	1.491(8)
S2−O17	1.414(4)	C2−C16	1.553(9)
S2−O18	1.439(5)	C3−C19	1.489(8)
S2−O19	1.395(6)	C5−C6	1.478(8)
S2−C21	1.812(7)	C8−C9	1.492(8)
F1−C20	1.298(8)	C11−C12	1.495(8)
F2−C20	1.308(7)	C14−C15	1.496(8)
F3−C20	1.331(8)	C16−C17	1.509(8)
F4−C21	1.307(8)	C17−C18	1.52(1)
F5−C21	1.317(9)	C18−C19	1.52(1)
F6−C21	1.272(9)		
	Bond Angles		
O1−Mn−O4	71.6(1)	O17−S2−C21	102.1(3)
O1−Mn−O7	142.8(1)	O18−S2−O19	115.3(3)
O1−Mn−O10	145.3(1)	O18−S2−C21	102.6(3)
O1−Mn−O13	73.8(1)	O19−S2−C21	103.7(3)
O1−Mn−O14	87.7(1)	O1−C2−C3	105.0(4)
O1−Mn−O17	87.8(1)	O1−C2−C16	112.5(5)
O4−Mn−O4	71.5(1)	C3−C2−C16	111.8(5)
O4−Mn−O10	142.4(1)	O4−C3−C2	107.5(4)
O15−S1−C20	104.2(3)	O4−C3−C19	109.9(4)
O16−S1−C20	103.2(3)	C2−C3−C19	113.8(5)
O17−S2−O18	114.6(3)	O4−C5−C6	106.9(5)
O17−S2−O19	115.7(3)	O7−C6−C5	108.6(5)

The seven Mn−O bond lengths range from 2.149(3) to 2.276(3) Å, and the variation in the distance to crown oxygen atoms suggests that the Mn(II) ion is not quite large enough to fill the crown cavity. The bond lengths and angles in the molecules are normal, though the S−O bonds involved in coordination to the Mn(II) ion are slightly elongated. Thermal motions are all reasonable, with the terminal F atoms moving most, as would be expected.

Discussion

We interpret our results in terms of a ligand displacement reaction as illustrated in Scheme 1, where ligands S may be a combination of water, PC, and possibly anions. The structures of $Mn(C15C5)(CF_3SO_3)_2$ (Figure 2) and $[Mn(C15C5)(DtBNS)(H_2O)](DtBNS)\cdot C_7H_8$[8] demonstrate the propensity of Mn(II) to be bound within the C15C5 cavity, and infrared results[12,14] suggest that this occurs in nonaqueous solution as well, even under wet conditions. We presume that the initial Mn(II) species is six-coordinate orthoaxial and that both reactant and product

Scheme 1



S = H_2O, PC, $CF_3SO_3^-$, or NO_3^-; L = C15C5

species adopt the high-spin configuration ($3d^5$).[20] Since no change in ligand-field stabilization energy occurs, the metal behaves as a pseudo alkaline earth.

Although relatively low water concentrations were employed here, the apparent effect of water on the thermodynamic parameters for the nitrate system (Figure 1) suggests that an increasing degree of hydration of the metal ion occurs with increasing water concentration. Solvations of the metal ion, free ligand, and metal–ligand complex all must be considered in a comprehensive treatment, but the solvation of the metal ion often dominates.[21] Accordingly, the increasingly positive ΔH and $T\Delta S$ terms on increasing the water concentration point to the disruption of an increasingly strong and structured solvation environment around the metal cation by the complexation process. Support for this conclusion may be found in studies of transition metal ions in the related aprotic protophobic solvent acetonitrile. In such solutions, water preferentially solvates Cu^{2+} ions[22,23] (no crown ether present) and presumably any of the divalent first-row metal ions. Preferential hydration has been suggested[6] as the reason that stability constants for Ni^{2+} and Zn^{2+} complexes of B15C5 in acetonitrile–water mixtures fall dramatically with increasing water content. In the case of Zn^{2+} complexation, the log K values fall 4 orders of magnitude as the water content is raised to 10 wt %. For Mn^{2+} ions in wet PC, Table 2 shows slight if any change in log K, but the range of our experiments extended only to the much lower water concentration of 134 mM (0.2 wt %).

The competing effect of water in the complexation of the first-row transition metal ions by crown ethers was also observed in solvent-extraction systems.[12,14] In particular, the water-solubilization ability of water-immiscible solvents containing a lipophilic Mn(II) salt decreases markedly upon complexation of the metal by the crown ether tBC15C5 or C15C5. Drying such solvents enhances the extent of complexation for all of the metals Mn(II)–Zn(II), though Mn(II) and Zn(II) are the only divalent metals in the series that retain the ability to coordinate significantly to these crown ethers when the solvent is water saturated.

On extrapolation to zero water content (Figure 1), the results for nitrate and triflate become essentially identical, in line with electrostatic principles (Bjerrum) that predict ion pairing to be minor for dilute divalent metal salts in PC (dielectric constant $\epsilon = 66.1$ at 25 °C).[24] Within the bounds of the limited data available,[23,25] association of anions of weak complexing ability with crown ether complexes of metal ions is generally less than the association with the corresponding uncomplexed metal ions. The fact that only the nitrate salt gives an appreciable change of enthalpy and entropy values with change in water content suggests that hydration of the nitrate ion, possibly mediated by metal ion-induced polarization of water,[23,26] must be more important than hydration of the triflate ion in PC.

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Supplementary Material Available: Listings of calculated atomic coordinates for hydrogen atoms, anisotropic thermal parameters, bond distances and angles, and deviations from the least-squares plane (6 pages). Ordering information is given on any current masthead page.

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(20) As will be reported elsewhere,[13] magnetic susceptibility measurements of the C15C5 complex of Mn(II) in acetonitrile indicate that no spin pairing occurs.

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