

Spectroscopy of multiply charged metal ions: Infrared studies of

$Mn^{2+}(18\text{-crown-6})(CH_3OH)_{1-3}$

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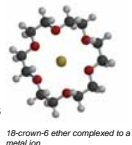
Abstract

Crown ethers are molecules that exhibit the ability to bind metal ions in solution **selectively**. Gas-phase experiments provide a suitable avenue to study this **selectivity** from a fundamental level. We have used infrared spectroscopy combined with density functional theory calculations to study the step-wise micro-solvation of $Mn^{2+}(18\text{-crown-6})$ by 1–3 CH_3OH molecules. Insight gained from this study may shed light on the molecular basis behind the **selectivity** exhibited in solution and provide the basis for the design and development of **highly-selective ionophores**.



Motivation

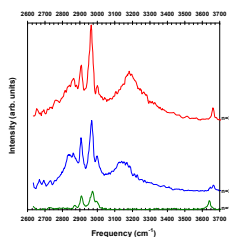
- Ionophores sequester ions in solution **selectively**
- Useful for ion extraction in industrial and environmental processes
- The balance of various non-covalent effects determines **selectivity**
 - ion-ionophore
 - solvent-ionophore
 - ion-solvent
 - solvent-solvent



Classical Prototypes: Crown Ethers

18-crown-6 ether complexed to a metal ion.

IR spectra of $Mn^{2+}(18\text{-crown-6 ether})(CH_3OH)_n$



Intense features in both O—H stretch region and C—H stretch region.

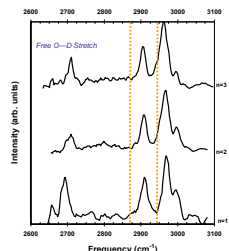
In the 2800–3000 cm^{-1} , C—H stretches from 18c6 and CH_3OH are present and overlap.

Hydrogen-bonded O—H stretches may also be red-shifted to this spectral region.

Question: How can we resolve these features?

Solution: Prepare clusters with d_1 and d_2 methanol.

IR spectra of $Mn^{2+}(18\text{-crown-6 ether})(CD_3OD)_n$



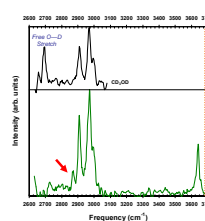
Use of CD_3OD allows for unambiguous identification of 18c6 methylene stretches.

Neutral free-18c6 has C—H symmetric and asymmetric vibrations at 2870 and 2940 cm^{-1} , respectively.

C—H stretches of 18c6 in solvated $Mn^{2+}(18c6)$ complexes shift to higher frequencies (sym. ~2900 cm^{-1} and asym. ~2960 cm^{-1}).

Feature at ~2700 cm^{-1} belongs to free O—D stretch.

$Mn^{2+}(18\text{-crown-6 ether})(methanol)_1$



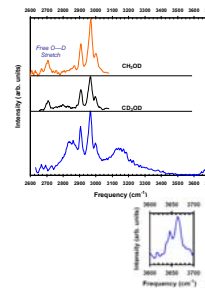
Free O—H stretch is red shifted ~40 cm^{-1} compared to gas-phase neutral value⁹ of 3681 cm^{-1} (shown by dotted line).

No evidence hydrogen-bonded O—H stretches below 3600 cm^{-1} .

Overlap with 18c6 C—H stretches preclude individual assignments of CH_3OH C—H vibrations, but the feature at 2880 cm^{-1} is likely the ν_3 C—H stretching mode in CH_3OH .

⁹J. Chem. Phys. 95, 3524 (1991)

$Mn^{2+}(18\text{-crown-6 ether})(methanol)_2$



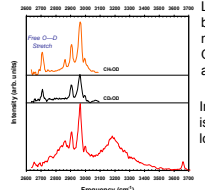
Intense O—H hydrogen-bonding seen below 3600 cm^{-1} , for d_0 -methanol only!

In addition to hydrogen-bonded O—H stretch centered at 3150 cm^{-1} , there is another broad feature centered at 2850 cm^{-1} , not present in any of the deuterated spectra.

Broad feature at 2850 cm^{-1} can only be due to a **hydrogen bonded O—H stretch**.

A zoom-in of the free O—H region clearly show two distinct free-OH stretches.

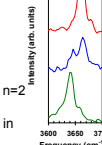
$Mn^{2+}(18\text{-crown-6 ether})(methanol)_3$



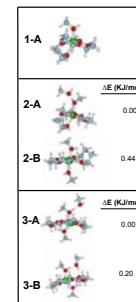
Like in $n=2$, there seems to be two broad hydrogen-bonded O—H features not present in the deuterated species. One is again below 3000 cm^{-1} while another is centered at 3180 cm^{-1} .

In free O—H region there is only a single peak located at 3663 cm^{-1} .

The free-O—H progression is quite interesting. The $n=2$ spectrum is a "transitional" spectrum as the lower frequency peak (seen in $n=1$) diminishes in intensity in favor of the higher frequency peak (seen in $n=3$).



Possible Structures



Fully optimized structures found for each size using DFT methods in *Gaussian 03* suite.

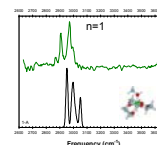
For $n=1$, Mn^{2+} prefers to be coordinated by all six crown ether oxygens. Methanol binds directly to ion.

For $n=2$, two isomers are nearly isoenergetic. *methanol—methanol (2-A)* and *methanol—18c6 hydrogen bonding (2-B)* are predicted in these structures.

For $n=3$, **3-A** features methanols on both sides of the 18c6 while **3-B** features all methanols tied up in hydrogen bonds.

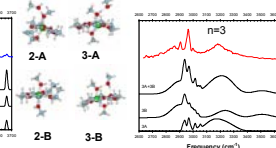
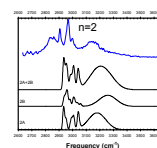
As solvent is added, 18c6 structure becomes more planar, mimicking its structure in the condensed-phase.

BSL YPB-314-D* Optimized Geometries using LANL20Z ECP on Mn orbitals.



There is reasonable agreement between calculated and experimental spectra for $n=1$ and 3.

The agreement between experiment and calculations is not nearly as good for $n=2$. The broad band below 3000 cm^{-1} and the doublet in the free O—H region are not reproduced. This suggests that there may be additional isomers not yet found.



Summary

$Mn^{2+}(18c6)(CH_3OH)_{1-3}$ complexes have been generated via ESI and probed by IR Laser Spectroscopy.

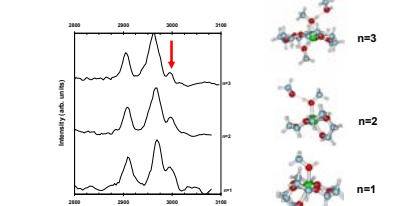
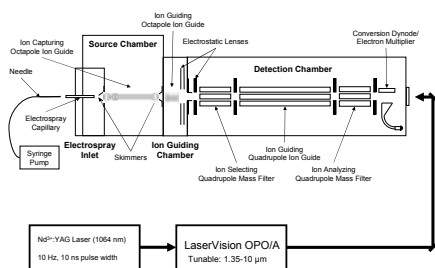
We have obtained spectra in the C—H and O—H stretching regions. With the aid of deuterated methanol and DFT calculations we have been able to deconvolute and identify 18c6 C—H stretches and CH_3OH C—H and O—H stretches.

The strong Mn^{2+} —18c6 interaction causes a distortion in 18c6 which is detected in the features observed in the C—H stretch region and in the optimized geometries.

Hydrogen bonding plays an important role in these complexes as both *methanol—methanol* and *methanol—18c6* interactions are observed for $n=2,3$.

DFT calculations as of yet have been unable to fully explain the $n=2$ spectra. Further studies are in progress.

Apparatus



The feature at ~3000 cm^{-1} is likely due to methylene group(s) perturbed by the strong Mn^{2+} —18c6 interaction. Increased solvent number reduces the distortion as CH_3OH binds to Mn^{2+} , allowing 18c6 to assume a more planar configuration (as seen above).

Acknowledgements

- NSF Grant CHE-0415859
- NSF CRIF 05-41659
- Donors of ACS-PRF
- NCSA Grant TG-CHE070097