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Communication

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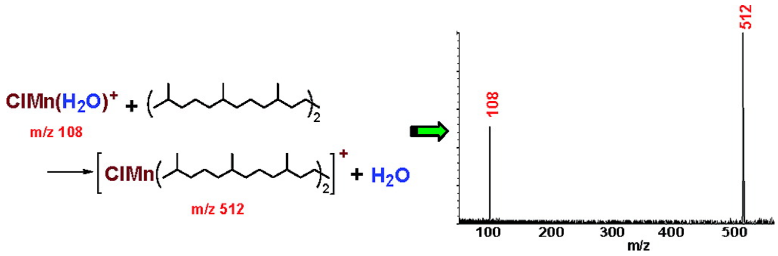

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Gas-Phase Reactions of $ClMn(H_2O)^+$ with Polar and Nonpolar Hydrocarbons in a Mass Spectrometer

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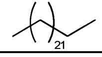
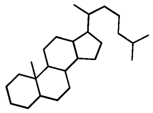
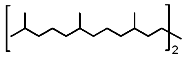
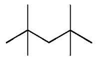
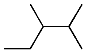
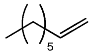
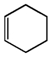
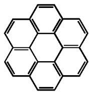
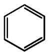
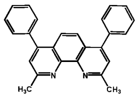
The ability to use mass spectrometry in the characterization of nonpolar hydrocarbons and their mixtures, such as synthetic saturated hydrocarbon polymers and the nonpolar components of petroleum, is highly desirable because this method yields both structural as well as molecular weight (MW) information.[1] However, saturated hydrocarbons are notoriously difficult to analyze by mass spectrometry owing to a lack of ionizable functional groups. The few methods that are known to afford ionization of these compounds tend to cause dissociation which results in the loss of MW information.[1] In the search for better ionization methods for hydrocarbons, the reactivity of bare and ligated gas-phase transition metal ions (e.g., Fe^+, Ni^+, Ag^+, $FeCH_3^+$, and $CpCo^+$; Cp $= \eta^5$-cyclopentadienyl) has attracted interest.[2−9] The $CpCo^+$ ion has been reported to ionize most hydrocarbons without excessive fragmentation. It reacts with many alkanes by C−H bond insertion, predominantly yielding adduct ions that have lost one or two molecules of H_2.[4c,6−8] These product ions provide MW information although the extent of unsaturation may be difficult to determine (e.g., cyclohexene loses H_2 and cyclohexane loses $2H_2$, thus yielding the same product ion). Also, loss of cyclopentadiene (CpH), sometimes accompanied by an additional H_2 loss, has been observed for higher MW alkanes (C_nH_{2n+2}, $n > 20$).[4c] Moreover, some alkanes undergo C−C bond cleavages upon reactions with $CpCo^+$ (e.g., loss of C_2H_4, C_3H_6, C_4H_8, or $CH_3^\bullet$).[4a,8] Hence, a less aggressive reagent ion is desirable. We report here on the gas-phase reactions of such an ion, a ligated water cluster of Mn^+: $ClMn(H_2O)^+$.

The $ClMn(H_2O)^+$ ions were generated by electron ionization (30 eV electron energy, 7 μA emission current, 80 ms ionization time) of $MnCl(CO)_5$ (synthesized[10] from $Mn_2(CO)_{10}$ by reaction with Cl_2 in CCl_4) in the presence of H_2O vapor in one cell of a Finnigan dual-cell Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR). The ions were transferred into the other cell and isolated before reactions with neutral compounds. Volatile hydrocarbons were introduced via an adjustable leak valve. Nonvolatile hydrocarbons were dissolved in tetrahydrofuran, electrospray-deposited on a titanium foil, and evaporated by using laser-induced acoustic desorption[11] (LIAD) as described earlier.[11e,f]

The isolated $ClMn(H_2O)^+$ ions were allowed to react with a variety of hydrocarbons typical of those that commonly exist in petroleum. Remarkably, every compound studied yields only one product ion (Table 1). This is true even for those compounds that undergo skeletal fragmentation upon reactions with $CpCo^+$ (e.g., 5-α-cholestane and tetrahydrofuran).[8] The product ion is formed by replacement of H_2O in $ClMn(H_2O)^+$ by the hydrocarbon.

Table 1. Products Formed in Reactions of $ClMn(H_2O)^+$ with a Variety of Compounds Typical of Those Present in Petroleum

Hydrocarbon (MW)	**Chemical Structure**	**Products, *m/z***
Linear alkane [a] *Tetracosane* (338)		Adduct-H_2O, 428
Cyclic alkane [a] *5-α-Cholestane* (372)		Adduct-H_2O, 462
Branched alkanes *Squalane* (422) [a]		Adduct-H_2O, 512
2,2,4,4-Tetramethylpentane (128) [b]		Adduct-H_2O, 218
2,3-Dimethylpentane (100) [b]		Adduct-H_2O, 190
Alkenes [b] *1-Octene* (112)		Adduct-H_2O, 202
Cyclohexene (82)		Adduct-H_2O, 172
Aromatic *Coronene* (300) [a]		Adduct-H_2O, 390
Benzene (78) [b]		Adduct-H_2O, 168
Thiophene [b] *Tetrahydrothiophene* (88)		Adduct-H_2O, 178
Furan [b] *Tetrahydrofuran* (72)		Adduct-H_2O, 162
Nitrogen containing hydrocarbon [a] *2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline* (360)		Adduct-H_2O, 450

[a] Introduction via LIAD. [b] Introduction via an adjustable leak valve.

The H_2O replacement reaction is fast. For example, the reaction efficiencies[12] for benzene and 2,2,4,4-tetramethylpentane are 70% and 31%, respectively. This can be rationalized on the basis of the electronic structure of $ClMn^+$.[13a] The Mn^+-Cl bond involves the one readily available electron ($4s^1$) in Mn^+ (ground electronic state $3d^54s^1$), leaving the rest of the valence electrons in Mn^+ in a high-spin d^5 configuration.[13b] Additional bond formation requires the disruption of this stable half-filled shell.[13] Hence, H_2O in $ClMn(H_2O)^+$ is weakly bound and should be readily replaced by many molecules. Indeed, this is the only reaction observed for the hydrocarbons studied. Further reactions within the $ClMn^+$/hydrocarbon complex do not take place because the ground-state $ClMn^+$ is not particularly reactive toward hydrocarbons for the reasons discussed above. The only reaction of $ClMn^+$ with small hydrocarbons reported in the literature is a slow replacement of the Cl atom (i.e., most of the $ClMn^+$/alkane complexes dissociate to $ClMn^+$ and alkane, as expected).[13a] This reaction does not occur for $ClMn(H_2O)^+$ because H_2O loss lowers the energy of the system.

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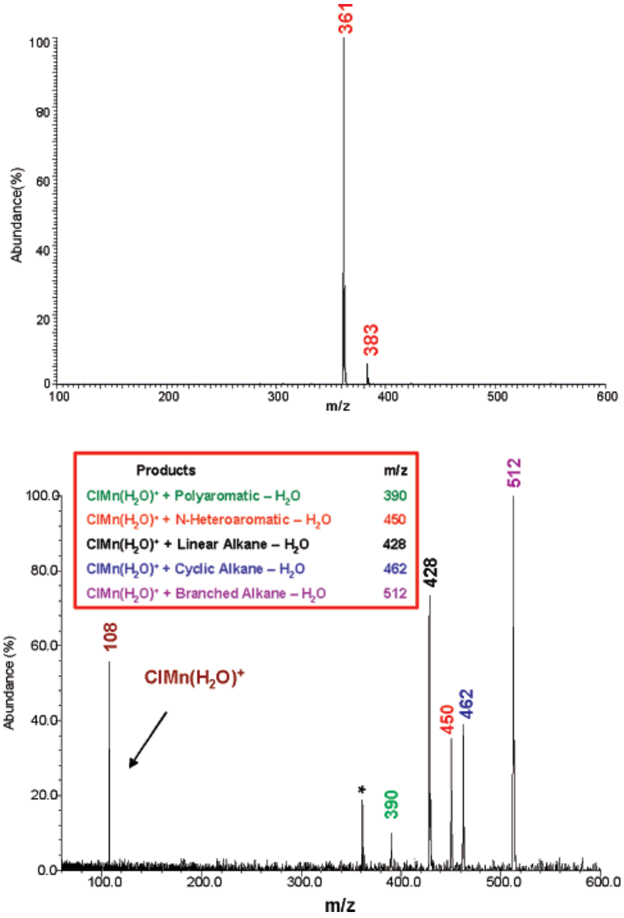

Figure 1. Comparison of ESI (top) and LIAD/$ClMn(H_2O)^+$ (bottom) mass spectra of a five-component mixture (~1:1:1:1:1) containing tetracosane (MW 338), 5-α-cholestane (MW 372), coronene (MW 300), squalane (MW 422), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (MW 360). The top spectrum shows signals only for the protonated and sodiated 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (*m*/*z* of 361 and 383, respectively). The bottom spectrum shows a signal for the $ClMn^+$ adduct for each of the five compounds. $*$ indicates chemical noise.

Sustained off-resonance irradiated collision-activated dissociation[14] (SORI-CAD) was used to examine the dissociation reactions of the $ClMn^+$ complexes of 2,2,4,4-tetramethylpentane, 2,3-dimethylpentane, and 1-octene, as well as toluene, *n*-octane, and *n*-nonane. The $ClMn^+$ complexes of the last three compounds dissociate to form $ClMn^+$, as expected. However, the $ClMn^+$ complexes of the branched hydrocarbons 2,3-dimethylpentane and 2,2,4,4-tetramethylpentane lose ClMnH or $ClMnCH_3$, respectively, to yield especially stable *tertiary* carbocations. The 1-octene complex predominantly loses ClMnH to yield a stable allyl cation. 1-Octene loss is also facile. However, the 1-octene complex also dissociates by loss of five other alkenes, C_2H_4, C_3H_6, C_4H_8, C_5H_{10}, or C_6H_{12}, of which C_5H_{10} loss dominates (corresponding to cleavage of the weak allylic C−C bond). These dissociation patterns are intriguing because they provide structural information for the hydrocarbons complexed with $ClMn^+$; that is, presence and type of branching, presence of unsaturation, and possibly location of unsaturation. The potential of using these reactions to distinguish and identify isomeric hydrocarbons will be explored in the future.

Finally, a mixture of tetracosane (a linear alkane), 5-α-cholestane (a cyclic alkane), squalane (a branched alkane), coronene (a polyaromatic hydrocarbon), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (a N-heteroaromatic compound) (all in equimolar ratios) was evaporated by LIAD and allowed to react with $ClMn(H_2O)^+$. The resulting mass spectrum shows the H_2O replacement product for every component of the mixture (Figure 1, bottom). While the relative product ion abundances do not exactly match the relative molar concentration of each mixture component, they are still remarkably close when considering the fact that the compositions, structures, and volatilities of the compounds vary widely. In sharp contrast, electrospray ionization (ESI; performed on a Finnigan linear quadrupole ion trap (LTQ) mass spectrometer) only reveals the presence of the most polar mixture component, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Figure 1, top).

In conclusion, $ClMn(H_2O)^+$ efficiently ionizes various types of hydrocarbons, both polar and nonpolar, as well as other compounds typically present in petroleum, to exclusively form pseudomolecular ions (adduct-H_2O). Even highly branched hydrocarbons yield solely this product ion when exposed to $ClMn(H_2O)^+$. Collisional activation of these product ions yields structural information on the hydrocarbons and may allow distinction and identification of isomeric hydrocarbons.

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References

(1) See for example: (a) Bricker, Y.; Ring, Z.; Iacchelli, A.; McLean, N.; Malhortra, R.; Coggiola, M. A.; Young, S. E. *Energy Fuels* **2001**, *15*, 996−1002. (b) Schaub, T. M.; Linden, H. B.; Hendrickson, C. L.; Marshall, A. G. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 1641−1644. (c) Montaudo, G.; Lattimer, R. P. *Mass Spectrometry of Polymers*; CRC Press: Boca Raton, FL, 2002.

(2) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121−1171.

(3) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3900−3904.

(4) (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 7399−7407. (b) Ekeberg, D.; Uggerud, E.; Lin, H.-Y.; Sohlberg, K.; Chen, H.; Ridge, D. P. *Organometallics* **1999**, *18*, 40−44. (c) Byrd, H. C. M.; Guttman, C. M.; Ridge, D. P. *J. Am. Soc. Mass Spectrom.* **2003**, *14*, 51−57.

(5) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527−569.

(6) Campbell, J. L.; Crawford, K. E.; Kenttämaa, H. I. *Anal. Chem.* **2004**, *76*, 959−963.

(7) Campbell, J. L.; Fiddler, M. N.; Crawford, K. E.; Gqamana, P. P.; Kenttämaa, H. I. *Anal. Chem.* **2005**, *77*, 4020−4026.

(8) Crawford, K. E.; Campbell, J. L.; Fiddler, M. N.; Duan, P.; Qian, K.; Gorbaty, M. L.; Kenttämaa, H. I. *Anal. Chem.* **2005**, *77*, 7916−7923.

(9) Kahr, M. S.; Wilkins, C. L. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 453−460.

(10) Reimer, K. J.; Shaver, A. *Inorg. Synth.* **1990**, *28*, 154−159.

(11) (a) Lindner, B.; Seydel, U.; *Anal. Chem.* **1985**, *57*, 895−899. (b) Lindner, B. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *103*, 203−218. (c) Golovlev, V. V.; Allman, S. L.; Garrett, W. R.; Chen, C. H. *Appl. Phys. Lett.* **1997**, *71*, 852−854. (d) Golovlev, V. V.; Allman, S. L.; Garrett, W. R.; Taranenko, N. I.; Chen, C. H. *Int. J. Mass Spectrom. Ion Proc.* **1997**, *169/170*, 69−78. (e) Petzold, C. J.; Ramirez-Arizmendi, L. E.; Heidbrink, J. L.; Kenttämaa, H. I. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 192−194. (f) Perez, J.; Ramirez-Arizmendi, L. E.; Petzold, C. J.; Guler, L. P.; Nelson, E. D.; Kenttämaa, H. I. *Int. J. Mass Spectrom.* **2000**, *198*, 173−188.

(12) Reaction efficiencies reported in this work are defined as $k_{reaction}/k_{collision} \times 100\%$ (i.e., the percent of collisions that are reactive). See: Price, J. M.; Kenttämaa, H. I. *J. Phys. Chem. A* **2003**, *107*, 8985−8995.

(13) (a) Mandich, M. L.; Steigerwald, M. L.; Reents, Jr., W. D. *J. Am. Chem. Soc.* **1986**, *108*, 6197−6202. (b) Armentrout, P. B.; Beauchamp, J. L. *Acc. Chem. Res.* **1989**, *22*, 315−321.

(14) Gauthier, J. W.; Trautman, T. R.; Jacobson, D. B. *Anal. Chim. Acta* **1991**, *246*, 211−225.

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