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Transition-Metal Cluster Ions in the Gas Phase. Oxide Chemistry of Dimeric and Trimeric Clusters Containing Iron and Cobalt

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Abstract: The oxide chemistry of both dimeric and trimeric transition-metal cluster ions containing iron and cobalt was studied in the gas phase by using Fourier transform mass spectrometry (FTMS). The dimers Fe_2^+, $CoFe^+$, and Co_2^+ react rapidly with ethylene oxide by sequentially abstracting two oxygen atoms, while the trimers $FeCo_2^+$ and Co_3^+ abstract up to three oxygen atoms from ethylene oxide. The dimers and trimers also react with dioxygen. In addition, the bimetallic carbonyl cations $Fe_2(CO)_4^+$, $CoFe(CO)_3^+$, and $Co_2(CO)_3^+$ react rapidly with dioxygen by displacing all the carbonyls forming $M'MO_2^+$ exclusively. The trimetallic carbonyl cations $FeCo_2(CO)_5^+$ and $Co_3(CO)_6^+$ react rapidly with dioxygen by displacing up to four carbonyls to generate $M'M_2(O)_2(CO)_n^+$ ($n = 1-3$). These species undergo a subsequent reaction with dioxygen which displaces the remaining carbonyls to generate both $M'M_2O_4^+$ and $M'M_2O_3^+$. The $M'M_2O_4^+$ species subsequently transfers an oxygen atom to dioxygen to generate $M'M_2O_3^+$ and presumably O_3. No fragmentations were observed for collisional activation of the $M'MO^+$, while the $M'MO_2^+$ species yielded M^+ and $M'MO^+$ in low efficiency, the $M'M_2O_3^+$ species yielded M^+ and $M'MO^+$ in very low efficiency, and the $M'M_2O_4^+$ species yielded $M'M_2O_3^+$. Finally, the observed ion-molecule reactions yield $D°(M'M^+\text{-}O) > 119$ kcal/mol, 204 kcal/mol $< D°(M'M^+\text{-}2O) <$ 238 kcal/mol, $D°(M'M_2^+\text{-}O) > 85$ kcal/mol, $D°(M'M_2O^+\text{-}O) > 85$ kcal/mol, $D°(M'M_2O_2^+\text{-}O) > 85$ kcal/mol, and $D°(M'M_2O_3^+\text{-}O) < 25.5$ kcal/mol. These results suggest formation of bridged oxide species for $M'MO^+$, $M'MO_2^+$, and $M'M_2O_3^+$.

There is considerable interest in small transition-metal clusters[1] since they are important in a variety of processes including homogeneous nucleation[2] and are of particular relevance to the study of catalytic activity.[3] As a result, these clusters have been the focus of intense experimental[4-13] and theoretical[14] investigations yielding information on such physical properties as structure, electronic character, binding energy, ionization potential, and electron affinity.

Due to their very nature, gas-phase ion techniques are ideally suited for studying size-selected metal cluster ions. Knudsen cell mass spectrometry has yielded bond energies for most homonuclear transition-metal dimers.[15] Armentrout and co-workers have also demonstrated the utility of using an ion beam instrument to determine the bond energy of dimer ions by measuring their collision-induced dissociation thresholds.[16]

In general transition-metal cluster ions have been generated by either electron impact[17] or multiphoton ionization,[18] typically on multinuclear carbonyl complexes. The former method, for example, has been employed for studying the gas-phase ion chemistry of Co_2^+ [19] and Mn_2^+ [19-21] by ion cyclotron resonance (ICR) spectrometry and ion beam techniques. These ionization techniques, however, are quite limited as to both the size and stoichiometry of the bare transition-metal cluster ions which can be generated. Smalley[10] and Bondybey[11] have recently developed elegant and convenient techniques for generating clusters of various sizes for gas-phase studies involving laser vaporization of metallic substrates in a helium stream. In addition, we recently demonstrated a new technique for generating transition-metal cluster ions in the gas phase.[22] The technique involves a two-step process in which the initial step is a gas-phase ion-molecule reaction between an atomic transition-metal ion and a transition-metal carbonyl complex in which one or more carbonyls are displaced.[23] Next, collisional activation[24] of the resulting ion sequentially strips the remaining carbonyls from the complex, ultimately producing the bare metal cluster ion. This technique is ideal for generating both homonuclear and heteronuclear dimeric[22] and trimeric[25] cluster ions. Using a combination of collision-induced dissociation, photodissociation, and ligand displacement reactions, the bond energies of a variety of homonuclear and heteronuclear dimeric transition-metal ions have been bracketed.[22,26]

Table I. Summary of New Thermochemical Data Discussed in the Text (in kcal/mol)

ion	ΔH_f	$D°(M'M^+\text{-}O)$	$D°(M'O^+\text{-}M)$
Fe_2O^+	<257 ± 7	>119	>117 ± 8
Co_2O^+	<258 ± 7	>119	>120 ± 8
$CoFeO^+$	<256 ± 7	>119	>117 ± 8

ion	ΔH_f	$D°(M'M^+\text{-}2O)$
$Fe_2O_2^+$	215 ± 18	221 ± 17
$Co_2O_2^+$	216 ± 18	221 ± 17
$CoFeO_2^+$	214 ± 18	221 ± 17

ion	ΔH_f	$D°(M'M^+\text{-}M)$
$FeCo_2^+$	>315 ± 19	<102 ± 19
Co_3^+	>318 ± 19	<102 ± 19

ion	$D°(M'M_2^+\text{-}O)$	ion	$D°(M'M_2O^+\text{-}O)$
$FeCo_2O$	>85	$FeCo_2O_2^+$	>85
Co_3O^+	>85	$Co_3O_2^+$	>85

ion	$D°(M'M_2O_2^+\text{-}O)$	ion	$D°(M'M_2O_3^+\text{-}O)$
$FeCo_2O_3^+$	>85	$FeCo_2O_4^+$	<25
$Co_3O_3^+$	>85	$Co_3O_4^+$	<25

neutral	ΔH_f	$D°(M\text{-}2O)$	IP
FeO_2	<34 ± 7	>185 ± 7	>181 (7.86 eV)
CoO_2	<34 ± 7	>185 ± 7	>181 (7.86 eV)

This report extends our studies on gas-phase transition-metal cluster ions in the gas phase by describing the oxide chemistry

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of diatomic and triatomic cluster ions containing iron and cobalt. Previously, Armentrout et al. reported the reaction of Mn_2^+ with oxygen using an ion beam instrument.[21] In addition, studies on copper,[10] iron,[12] and nickel[12] cluster ions were complicated by formation of oxide peaks (M_nO^+, $M_nO_2^+$), although these species could also be attributed to neutral/neutral collisions or oxide contaminants.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry[27] and Fourier transform mass spectrometry (FTMS)[28] have been discussed at length elsewhere. All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail[29] and equipped with a 5.2 cm cubic trapping cell situated between the poles of a 15 in. Varian electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and includes a $^1/_4$ in. diameter hole in one of the transmitter plates which permits irradiation with various light sources. High-purity foils of the appropriate metals were supported on the opposite transmitter plate. Metal ions were generated by focussing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto the metal foil.[30]

Chemicals were obtained commercially in high purity and were used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. $Fe(CO)_5$ and $Co_2(CO)_8$ were introduced into the vacuum chamber at a static pressure of $\sim 3 \times 10^{-8}$ torr. The oxide reagents were added to bring the pressure to $1–3 \times 10^{-7}$ torr. Argon was used as the collision gas for collision-induced dissociation (CID)[24] at a total pressure of $\sim 5 \times 10^{-6}$ torr. A Bayard-Alpert ionization gauge was used to monitor pressure. Details of the CID experiments have previously been discussed.[29,31,32] The collision energy of the ions can be varied (typically between 0 and 100 eV).

The carbonyl dimers, $Fe_2(CO)_4^+$ and $CoFe(CO)_3^+$, were generated by reaction of laser desorbed Fe^+ and Co^+ with $Fe(CO)_5$, reactions 1 and 3. $Co_2(CO)_n^+$ (n = 0–8) ions where generated by electron impact on $Co_2(CO)_8$. The trimeric metal carbonyl cluster ions, $FeCo_2(CO)_5^+$ and $Co_3(CO)_6^+$, were generated by reaction of laser desorbed Fe^+ and Co^+ with $Co_2(CO)_8$, reactions 5 and 6. Collisional activation[29,31,32] of the products of reactions 1, 3, 5, and 6 results in sequential elimination of the carbonyls forming bare cluster ions, process 8. Process 8 undoubtedly generates bare cluster ions with a distribution of internal energies. The CID collision gas pressure was kept high ($\sim 5 \times 10^{-6}$ torr) relative to the reagent gas pressure ($1–3 \times 10^{-7}$ torr), therefore, in order to allow the excess energy to be dissipated by thermalizing collisions with argon prior to reaction.

$$Fe^+ + Fe(CO)_5 \xrightarrow{100\%} Fe_2(CO)_4^+ + CO \quad (1)$$

$$Co^+ + Fe(CO)_5 \xrightarrow{5\%} CoFe(CO)_4^+ + CO \quad (2)$$

$$Co^+ + Fe(CO)_5 \xrightarrow{95\%} CoFe(CO)_3^+ + 2CO \quad (3)$$

$$Fe^+ + Co_2(CO)_8 \xrightarrow{20\%} FeCo_2(CO)_6^+ + 2CO \quad (4)$$

$$Fe^+ + Co_2(CO)_8 \xrightarrow{80\%} FeCo_2(CO)_5^+ + 3CO \quad (5)$$

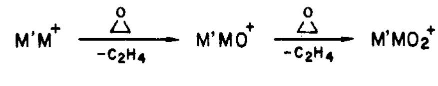
$$Co^+ + Co_2(CO)_8 \xrightarrow{72\%} Co_3(CO)_6^+ + 2CO \quad (6)$$

$$Co^+ + Co_2(CO)_8 \xrightarrow{28\%} Co_3(CO)_5^+ + 3CO \quad (7)$$

$$M'M_n(CO)_y^+ \xrightarrow{-CO} M'M_n(CO)_{y-1}^+ \xrightarrow{-(y-1)CO} M'M_n^+ \quad (8)$$

Results and Discussion

The bare diatomic ions (Fe_2^+, $CoFe^+$, Co_2^+) react rapidly with ethylene oxide by sequentially abstracting two oxygen atoms, reaction 9. This is in contrast to the corresponding atomic metal



$$M'M^+ \xrightarrow[-C_2H_4]{\overset{O}{\triangle}} M'MO^+ \xrightarrow[-C_2H_4]{\overset{O}{\triangle}} M'MO_2^+ \quad (9)$$

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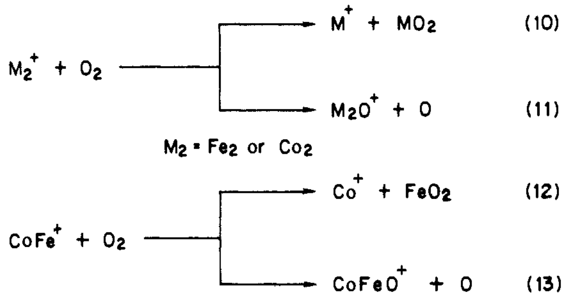
ions which predominantly form MCH_2^+ and MCO^+ with ethylene oxide.[33] Dioxygen reacts slowly with these dimers by reactions 10–13. Reactions 10 and 12 dominate over reactions 11 and 13 by roughly a 2:1 ratio. No further reactions with dioxygen are observed for the $M'MO^+$ species. Mn_2^+ has also been observed to undergo reactions 10 and 11 as exothermic processes in an ion beam instrument.[21]



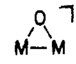
Reactions 11 and 13 imply $D°(M'M^+–O) > 119$ kcal/mol,[34] which is nearly twice that of the corresponding atomic species with $D°(Fe^+–O) = 68 \pm 3$ kcal/mol and $D°(Co^+–O) = 65 \pm 3$ kcal/mol.[35] This limit coupled with observation of reaction 9 and the absence of formation of $M'MO_2^+$ from $M'MO^+$ and dioxygen implies 204 kcal/mol < $D°(M'M^+–2O)$ < 238 kcal/mol[34] from which $D°(M'M^+ - 2O) = 221 \pm 17$ kcal/mol is assigned. These results yield $\Delta H_f(Fe_2O_2^+) = 215 \pm 18$ kcal/mol, $\Delta H_f(Co_2O_2^+) = 216 \pm 18$ kcal/mol, $\Delta H_f(CoFeO_2^+) = 214 \pm 18$ kcal/mol, $\Delta H_f(Fe_2O^+) < 257 \pm 7$ kcal/mol, $\Delta H_f(Co_2O^+) < 258 \pm 7$ kcal/mol, and $\Delta H_f(CoFeO^+) < 256 \pm 7$ kcal/mol.[34,36] In addition, these results imply $D°(FeO^+–Fe) > 117 \pm 8$ kcal/mol, $D°(CoO^+–Co) > 120 \pm 8$ kcal/mol, $D°(FeO^+–Co) > 117 \pm 8$ kcal/mol, and $D°(CoO^+–Fe) > 120 \pm 8$ kcal/mol[34,36] which are roughly twice that for $D°(M^+–M')$.[36] Reactions 10 and 12 imply $D°(Co–2O)$ and $D°(Fe–2O) > 185 \pm 7$ kcal/mol[34,36] in agreement with $D°(M–2O) > 200$ kcal/mol from an earlier study.[37] For comparison, $D°(Fe–O) = 93 \pm 4$ kcal/mol[38,39] and $D°(Co–O) = 87 \pm 4$ kcal/mol.[40,41] Finally, absence of MO_2^+ formation in reactions 10 and 12 implies $IP(MO_2) > IP(Co) = 7.86$ eV.[34,42] These results are summarized in Table I.

The oxygen-containing species N_2O, NO, CO, CO_2, H_2O, $(CH_3)_2O$, and $(CH_2)_4O$ were all unreactive with the above bare dimer ions. Absence of oxygen abstraction with N_2O, even though it is energetically very favorable,[34] suggests a kinetic barrier which may result from spin restrictions in the intermediate complex.[43] Beauchamp and co-workers observed a kinetic barrier for oxygen abstraction from N_2O by atomic transition-metal ions and attributed it to spin multiplicity differences.[44] Therefore, the upper limits for $D°(M'M^+–2O)$ must be viewed with caution.

Dioxygen reacts rapidly with $Fe_2(CO)_4^+$, $CoFe(CO)_3^+$, and $Co_2(CO)_x^+$ ($x = 1–3$) by displacing all the carbonyls forming $M'MO_2^+$ which is consistent with strong oxide bonds as suggested above. $Co_2(CO)_4^+$ and $Co(CO)_5^+$ react progressively more slowly, resulting in displacement of 3 carbonyls, exclusively, while $Co_2(CO)_{6-8}^+$ are unreactive with dioxygen. The $M'MO_2^+$ and $Co_2O_2(CO)^+$ ions are unreactive with dioxygen. Dioxygen reacts quite differently with $MCr(CO)_x^+$ (M = Mn, Co, Ni; x = 3, 4, 6) with condensation and elimination of MO_2 observed and with no carbonyl elimination occurring.[45] Recently, mononuclear transition-metal carbonyl anions were observed to react slowly and sequentially with dioxygen in the gas phase, yielding metal–carbonyl–oxide products.[46]

The above results for reaction of dioxygen with the dimeric cobalt carbonyl ions indicate that the degree of coordination dramatically affects the reactivity of these clusters with dioxygen. The fact that $Co_2(CO)_6^+$ is unreactive with dioxygen and that $Co_2(CO)_4^+$ and $Co_2(CO)_5^+$ react very slowly implies that these reactions proceed by initial dissociation of dioxygen followed by carbonyl elimination. Apparently, the $Co_2(CO)_6^+$ ion is too coordinatively saturated to allow for dioxygen dissociation forming a $Co_2(CO)_6(O)_2^+$ species. Meckstroth et al. have observed a similar effect in the clustering reactions of metal carbonyl fragment ions with the parent metal carbonyl compounds.[47]

No fragmentations were observed for CID of the $M'MO^+$ ions produced in reactions 9, 11, and 13 when accelerated to ~100 eV kinetic energy. CID of $M'MO_2^+$, formed in reaction 9 or by reaction of dioxygen with the bimetallic carbonyls, yields M^+ and $M'MO^+$ in very low efficiency in analogy to reactions 10–13 with dioxygen. These results, together with the above thermodynamics, suggest formation of the bridged oxide species, **1** and **2**, in analogy to bridging oxides commonly observed for transition-metal cluster oxide compounds.[48]



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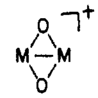

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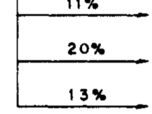
The trinuclear ions ($FeCo_2^+$ and Co_3^+) sequentially abstract three oxygen atoms from ethylene oxide, reaction 14. Dioxygen reacts rapidly with $FeCo_2^+$ and Co_3^+ to yield exclusive cleavage of the trimer framework, reactions 15–23. Reactions 19, 20, and 23 imply $D°(FeCo^+–Co)$, $D°(Co_2^+–Fe)$, and $D°(Co_2^+–Co)$ are all less than 101.5 ± 19 kcal/mol.[34] In addition, collisional activation of $FeCo_2^+$ yields both $FeCo^+$ and Co_2^+ in roughly a



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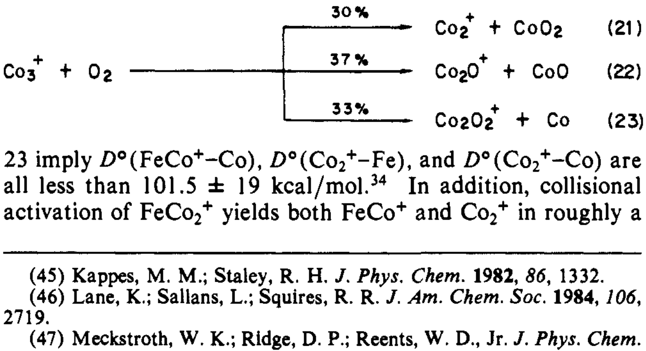

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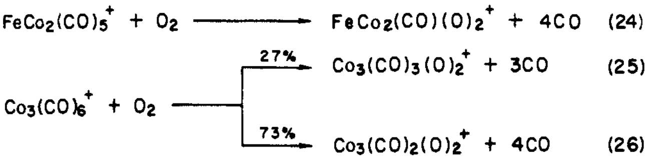
2:1 ratio suggesting $D°(FeCo^+–Co) \sim D°(Co_2^+–Fe)$.

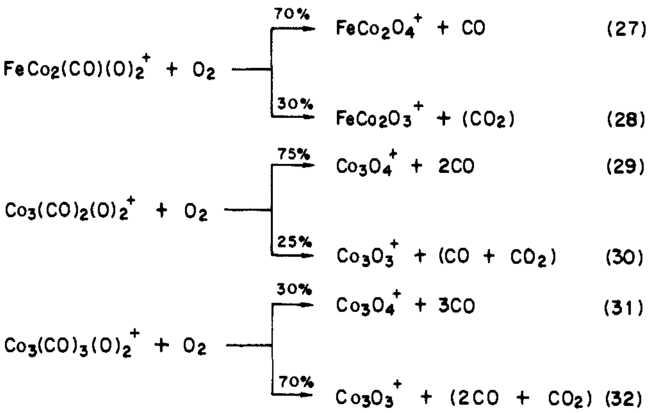
Dioxygen reacts rapidly with both $FeCo_2(CO)_5^+$ and $Co_3(CO)_6^+$, resulting in carbonyl eliminations, reactions 24–26. These products react a second time with dioxygen to yield reactions 27–32. Both the $FeCo_3(CO)(O)_2^+$ and $Co_3(CO)_2(O)_2^+$ reactions are rapid ($k > 5 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹) whereas the $Co_3(CO)_3(O)_2^+$ reaction is markedly slower ($k < 1 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹). This may be attributed once again to the higher degree of coordination in the latter case.



$$FeCo_2(CO)_5^+ + O_2 \longrightarrow FeCo_2(CO)(O)_2^+ + 4CO \quad (24)$$

$$Co_3(CO)_6^+ + O_2 \xrightarrow{27\%} Co_3(CO)_3(O)_2^+ + 3CO \quad (25)$$

$$Co_3(CO)_6^+ + O_2 \xrightarrow{73\%} Co_3(CO)_2(O)_2^+ + 4CO \quad (26)$$



$$FeCo_2(CO)(O)_2^+ + O_2 \xrightarrow{70\%} FeCo_2O_4^+ + CO \quad (27)$$

$$FeCo_2(CO)(O)_2^+ + O_2 \xrightarrow{30\%} FeCo_2O_3^+ + (CO_2) \quad (28)$$

$$Co_3(CO)_2(O)_2^+ + O_2 \xrightarrow{75\%} Co_3O_4^+ + 2CO \quad (29)$$

$$Co_3(CO)_2(O)_2^+ + O_2 \xrightarrow{25\%} Co_3O_3^+ + (CO + CO_2) \quad (30)$$

$$Co_3(CO)_3(O)_2^+ + O_2 \xrightarrow{30\%} Co_3O_4^+ + 3CO \quad (31)$$

$$Co_3(CO)_3(O)_2^+ + O_2 \xrightarrow{70\%} Co_3O_3^+ + (2CO + CO_2) \quad (32)$$

Both $FeCo_2O_3^+$ and $Co_3O_3^+$ are unreactive with dioxygen; however, the $M'M_2O_4^+$ species react according to eq 33. This

$$M'M_2O_4^+ + O_2 \rightarrow M'M_2O_3^+ + O_3 \quad (33)$$

implies that $D°(M'M_2O_3^+–O) < D°(O_2–O) = 25.5$ kcal/mol.[34] This compares with $D°(M'M_2O_2^+–O) > 85$ kcal/mol from reaction 14.[34] The weakness of the $M'M_2O_3^+–O$ bond is surprising since Fe_3O_4 and Co_3O_4 are much more stable oxides than Fe_3O_3 and Co_3O_3.[48]

Collisional activation of $Co_3O_4^+$ yields predominantly elimination of an oxygen atom forming $Co_3O_3^+$ with a small amount of CoO_2 elimination also observed. Collisional activation of $FeCo_2O_4^+$ is similar with O elimination forming $FeCo_2O_3^+$ dominating with a small amount of CoO_2 and FeO_2 elimination also observed. In contrast the $M'M_2O_3^+$ ions do *not* undergo fragmentation upon collisional activation at 75 eV kinetic energy suggesting that they are very stable. These $M'M_2O_3^+$ ions may consist of a triangular array of metals bridged by three oxides similar to structure **2**.

Conclusions

The oxide chemistry of these dimeric and trimeric cluster ions is much richer than that for the corresponding monomeric transition-metal ions. This is due in large part to the very strong oxide bonds in these clusters relative to the monomeric species. Armentrout and co-workers observed similar behavior for reaction of Mn_2^+ with dioxygen.[21] Although these limited results increase our understanding of small transition-metal clusters, clearly additional experimental and detailed theoretical studies are needed before these clusters are well understood.

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Silicon-29 NMR Structural Characterization of Two Novel Germanosilicate Cages in a Tetramethylammonium Germanosilicate Solution[†]

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Abstract: We have identified two novel germanium-substituted silicate cages in an aqueous tetramethylammonium germanosilicate solution by means of high-field (11.7 T) silicon-29 NMR spectroscopy, with ^{29}Si isotopic enrichment. Our results indicate that these anions exist in the form of a double four-membered ring (cubic octameric cage) and a double three-membered ring (prismatic hexameric cage), in which a single silicon site is replaced by germanium. Introduction of chemical shift nonequivalence by means of heteroatom incorporation leads to complex spin–spin splitting patterns, which may, however, be readily interpreted by means of two-dimensional homonuclear correlated spectroscopy (2D-COSY) or by spectral simulation. The ^2J couplings are 7.5 Hz in the double four-membered ring and 4.3 Hz in the double three-membered ring. A ^4J coupling of $\sim$1.0 Hz is also deduced for the double three-membered ring. These results represent the first solution NMR observation of heteroatom incorporation into silicate cages and provide a novel means for investigating the structures and stabilities of such species.

The structures of the various species formed during the hydrolysis of silica or various silicates are of interest for a number of reasons, including the mechanism(s) of the sol–gel process (used in glass manufacture), the nature of the species present in zeolite precursor solutions, and the nature of the species formed during the weathering of minerals.[1-3] We are interested in all three topics, and in this article we describe a novel nuclear magnetic resonance (NMR) spectroscopic approach to the determination

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