C(C_5H_5) distance of 2.400 (4) Å is slightly less than the distances of 2.46 Å in (C_5H_5)Nb(CO)[(C_6H_5)$_2$C$_2$]$_2$[5] and 2.45 Å in {(C_5H_5)Nb(CO)[(C_6H_5)$_2$C$_2$]}$_2$.[6] The Nb–C(C_5H_4) distances according to type are 2.443 (8) Å for Nb(1)–C(3), 2.333 (6) Å for Nb(1)–C(2), and 2.302 (5) Å for Nb(1)–C(1). There do not appear to be any systematic variations in the C–C ring distances, with the average distances being 1.422 (8) Å for the C_5H_4 rings and 1.406 (6) Å for the C_5H_5 rings, similar to frequently observed distances.[7] The Nb(1)–C(1)–Nb(2) bridge angle is 86.5 (2)°, while the dihedral angle between the Nb(1)C(1)Nb(2) and Nb(1)C(6)Nb(2) planes is 128 (1)°.

The presence of the Nb–Nb bond is consistent with the diamagnetism of the complex; the niobium atoms may be considered to be in a formal oxidation state of IV (corresponding to a d^1 electronic configuration). Perhaps the Nb–Nb bond length of 3.105 (5) Å can best be compared with the Ti–Ti distance of 3.110 (7) Å in [(C_5H_5)Ti(C_5H_4)Al(C_2H_5)$_2$]$_2$ which has similar bridging geometry.[3] The Mo–Mn length for a singly bridging C_5H_4 group in (C_5H_5)(CO)Mo(C_5H_4)Mn(CO)$_4$ is 2.961 Å.[2] Other Nb–Nb bond lengths observed are 2.74 in {(C_5H_5)Nb(CO)[(C_6H_5)$_2$C$_2$]}$_2$, where double bond character is postulated,[6] 2.85 Å in the [Nb$_6$Cl$_{12}$]$^{2+}$ cluster,[8] 2.86 Å in niobium metal,[9] and 3.31 Å in α-NbI$_4$.[10] A single bond value[11] of 3.20 Å is obtained with the niobium atom radius derived from the Nb–C(C_5H_5) distance (2.40–0.80). The short Nb(1)–Nb(2) and Nb(1)–C(6) distances observed here probably indicate "bent" bonds as required by the constraints of the bridging system (the Nb(2)–Nb(1)–C(1) and Nb(2)–Nb(1)–C(6) angles are 45.8 (2) and 47.7 (1)°, respectively).

An interesting detail of the bridging structure here is the geometry imposed upon the hydrogen atoms attached to C(2) and C(7). In addition to the close contact (ca. 1.9 Å), each hydrogen atom is positioned near the plane of the adjacent ring. Possibly, the combined steric and ring current effects cause this hydrogen to be shifted 1.7 ppm downfield from the other three C_5H_4 hydrogens as observed in the 220-MHz proton nmr spectra of the niobium and tantalum complexes.[1]

We believe the tantalocene dimer has the same structure as the niobocene dimer structure reported here, based on the very similar Hägg–Guinier X-ray powder patterns and spectral properties. Also, there is a strong possibility[12] that the structure of the titanocene dimer, [(C_5H_5)(C_5H_4)TiH]$_2$,[13] contains bridging C_5H_4 groups as found here. Brintzinger and Bercaw[13] proposed a double-hydrogen-bridged structure for the titanocene dimer. Additional supportive evidence for bridging C_5H_4 groups is the fact that the [(C_5H_5)Ti(C_5H_4)]$_2$ part of the [(C_5H_5)Ti(C_5H_4)Al(C_2H_5)$_2$]$_2$ structure[3] is

Figure 1. The front and top views of the molecular structure of [(C_5H_5)(C_5H_4)NbH]$_2$. The ring hydrogen atoms have been omitted.

practically identical with the structure found here. The [(C_5H_5)Ti(C_5H_4)Al(C_2H_5)$_2$]$_2$ framework is obtained in Figure 1 by replacing the hydride hydrogen atoms with Al(C_2H_5)$_2$ groups bridging the Ti(2)–C(1) and Ti(1)–C(6) type bonds.

L. J. Guggenberger,* F. N. Tebbe

Chemical Consequences of Strong Hydrogen Bonding in the Reactions of Organic Ions in the Gas Phase. Induced Fragmentation of Aliphatic Alcohols

Sir:

The strong hydrogen bond is formed when two n-donor bases are bound together by a proton. This functional group has recently received considerable attention from both an experimental[1–5] and theoretical

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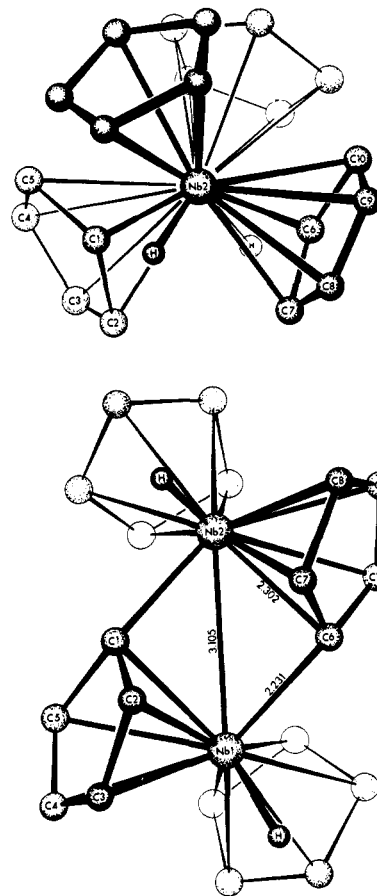(13) H. H. Brintzinger and J. E. Bercaw, J. Amer. Chem. Soc., 92, 6182 (1970), and references therein.

(1) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, J. Amer. Chem. Soc., 92, 7484 (1970).

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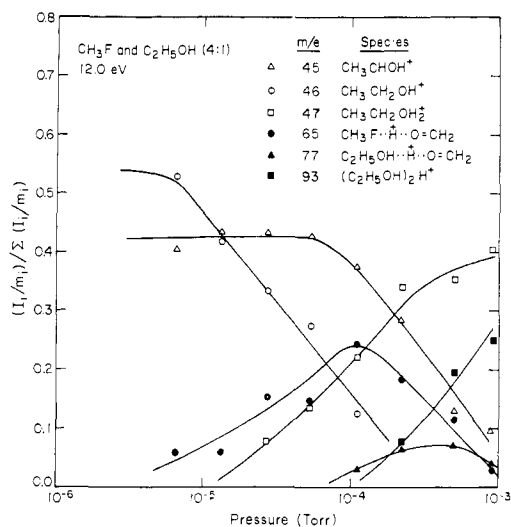(5) G. Ferguson, J. G. Sime, J. V. Speakman, and R. Young, Chem. Commun., 162 (1968).
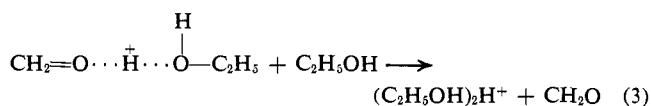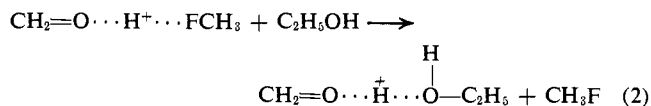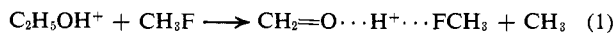
Figure 1. Variation with pressure of ion densities (reported as mass-corrected single-resonance intensities) for a 4:1 mixture of CH_3F and C_2H_5OH at 12.0 eV.

point of view.[6,7] In recent publications we have explored the importance of strong hydrogen bonding in a variety of processes involving organic ions in the gas phase, including both nucleophilic displacement[1] and acid-catalyzed elimination reactions,[2,3] using the techniques of ion cyclotron resonance spectroscopy.[8] We wish to report here the participation of the strong hydrogen bond in a variety of interesting and apparently general gas-phase decomposition reactions.

In a mixture of C_2H_5OH and CH_3F the only ions present at 12.0-eV electron energy are CH_3CHOH^+ and $C_2H_5OH^+$. As the pressure is raised, the prominent products observed include $C_2H_5OH_2^+$ and an ion at m/e 65 which is not observed in ethanol alone (Figure 1). Double-resonance experiments[6] identify $C_2H_5OH^+$ as the precursor to the ionic species at m/e 65. As the pressure is raised further, the ion at m/e 65 is observed to react sequentially to generate product ions at m/e 77 and 93. In a mixture of C_2D_5OH and CH_3F, the ion products at m/e 65, 77, and 93 are observed to shift to m/e 67, 84, and 103, respectively. These results can be rationalized by the sequence of reactions
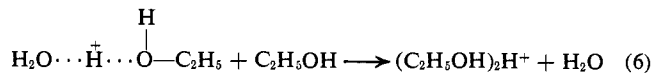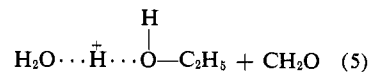
$$C_2H_5OH^+ + CH_3F \longrightarrow CH_2\!=\!O\cdots H^+\cdots FCH_3 + CH_3 \quad (1)$$

$CH_2\!=\!O\cdots H^+\cdots FCH_3 + C_2H_5OH \longrightarrow$

$$CH_2\!=\!O\cdots \overset{+}{H}\cdots \overset{H}{\underset{|}{O}}\!\!-\!\!C_2H_5 + CH_3F \quad (2)$$

$$CH_2\!=\!O\cdots \overset{+}{H}\cdots \overset{H}{\underset{|}{O}}\!\!-\!\!C_2H_5 + C_2H_5OH \longrightarrow$$
$$(C_2H_5OH)_2H^+ + CH_2O \quad (3)$$

To test the generality of reactions 1–3, a mixture of C_2H_5OH and H_2O was examined. Reactions 4–6 were

$$C_2H_5OH^+ + H_2O \longrightarrow CH_2\!=\!O\cdots H^+\cdots OH_2 + CH_3 \quad (4)$$
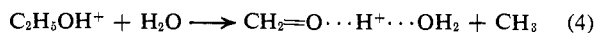
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$CH_2\!=\!O\cdots H^+\cdots OH_2 + C_2H_5OH \longrightarrow$

$$H_2O\cdots \overset{+}{H}\cdots \overset{H}{\underset{|}{O}}\!\!-\!\!C_2H_5 + CH_2O \quad (5)$$

$$H_2O\cdots \overset{+}{H}\cdots \overset{H}{\underset{|}{O}}\!\!-\!\!C_2H_5 + C_2H_5OH \longrightarrow (C_2H_5OH)_2H^+ + H_2O \quad (6)$$

identified by the variation of ion densities with pressure and double-resonance experiments. Further investigation using isotopically labeled $H_2{}^{18}O$ indicated retention of the label in accordance with the postulated sequence of reactions 4–6.[9]

Reactions 1 and 4 are examples of α-cleavage processes induced by the association of the alcohol parent ion with an n-donor base. Association of neutral alcohol with the parent ion of an n-donor base also leads to α cleavage. For example, the parent ion of acetone is observed to react with tert-butyl alcohol to yield the proton bound dimer of acetone (reaction 7).[10]

$$(CH_3)_2CO^+ + (CH_3)_3COH \longrightarrow [(CH_3)_2CO]_2H^+ + CH_3 \quad (7)$$
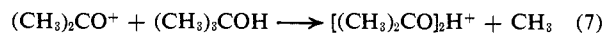
An examination of the thermochemistry of these processes is instructive. Since the energy threshold for production of CH_2OH^+ is 0.78 eV (18 kcal/mol) above the ionization potential of ethanol,[11] the hydrogen bond strength of the proton-bound dimers formed in reactions 1 and 4 must be greater than 18 kcal/mol.[12] A hydrogen bond strength for the proton-bound dimer of acetone in excess of 7 kcal/mol is required for reaction 7 to be exothermic. The limits set on the strength of the proton bond are entirely consistent with previous work which suggests that the hydrogen bond in proton-bound dimers has a strength of 25–40 kcal/mol (Table I).

Table I. Hydrogen Bond Strengths in Some Proton Bound Dimers

Process	$-\Delta H$, kcal/mol	Ref
$H_3O^+ + H_2O \rightarrow (H_2O)_2H^+$	32, 36	a, b
$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3OH)_2H^+$	31	c
$NH_4^+ + NH_3 \rightarrow (NH_3)_2H^+$	27	d

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Other features of the observed reactions are of interest. For example, in the decomposition of the parent ion of ethanol, the threshold for the formation of CH_3CHOH^+ is 0.31 eV below the threshold for the formation of CH_2OH^+.[11] The difference in these energy thresholds may be attributed to the stabilization of the carbonium ion center by the methyl group in CH_3CHOH^+. In the product of reactions 1 and 4, however, the charge density is redistributed in such a

(9) H_2O containing 40% ^{18}O was employed. The ionic products of reactions 4 and 5 retained all of the ^{18}O label. The ionic product of reaction 6 contained no ^{18}O.

(10) The postulated reaction has been substantiated by both isotopic labeling and examination of the subsequent reactions of the product ion. The neutral fragment CH_3 comes exclusively from the reactant alcohol.

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(12) The hydrogen bond strength in proton-bound dimers is defined as the enthalpy change for the process $M_1\cdots H^+\cdots M_2 \rightarrow M_1H^+ + M_2$ with the condition $PA(M_1) \geq PA(M_2)$; this gives the dissociation pathway of minimum energy.

manner as to reduce the stabilizing influence of the methyl group. For these reactions the energy threshold for C–C bond cleavage is apparently below that for C–H bond cleavage.[13]

An intriguing feature of the induced fragmentations exemplified in reactions 1, 4, and 7 is that they provide a convenient and facile means of generating proton-bound dimers for further investigation, including particularly displacement reactions. Hence it is of interest to note that even though the basicity of formaldehyde (as measured by its proton affinity) is greater than that of either methyl fluoride or water, ethanol preferentially displaces methyl fluoride in reaction 2 and formaldehyde in reaction 5.[14] Intermediate I would provide a particularly favorable (and noncompetitive) pathway for the displacement of

$$CH_2=O\cdots H\cdots O\begin{array}{c} H\cdots O-C_2H_5 \\ \diagdown \\ H \end{array}$$

I
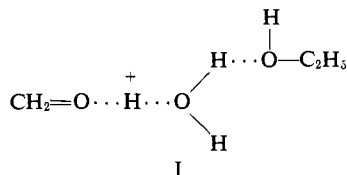
formaldehyde from the proton-bound dimer of formaldehyde and water.

It is apparent from these observations that the strong hydrogen bond plays an important role in bimolecular reactions. Decomposition processes are rendered exothermic by virtue of the unusual stability gained in the product ions by the formation of a strong hydrogen bond. We are currently investigating the generality of these processes as well as the chemistry of the proton-bound dimers which they produce.

(13) This argument does not imply that the methyl and hydrogen substituent effects are reversed. The proton affinity of CH₃CHO is 17 kcal/mol above that of CH₂O,[14] which may be attributed to stabilization of the carbonium ion center in CH₂OH⁺ by methyl substitution. The threshold for CH₃CHOH⁺ formation from CH₃CH₂OH⁺ is only 7 kcal/mol below the threshold for CH₂OH⁺ formation. Hence, it is necessary that the shift in charge density in the ionic product of reactions 2 and 4 reduce the methyl stabilization of the carbonium ion center to less than ~10 kcal/mol for C–C cleavage to become favored.

(14) The relevant proton affinities (kcal/mol) are: H₂O, 164;[15] CH₂O, 167;[11,15] CH₃CHO, 184;[11,15] and CH₃F, 151.[16]

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(18) Alfred P. Sloan Foundation Fellow, 1968–1970.

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Parallel Spin Coupling *via* a Three-Atom Covalent Bridge in Di-μ-thiocyanato-tetrakis(ethylenediamine)dinickel(II) Iodide

Sir:

In all of the known cases of parallel (*i.e.*, ferromagnetic) spin coupling in cluster complexes, *e.g.*, [Ni₃-(acac)₆][1] and [Ni₄(OCH₃)₄(acac)₄(CH₃OH)₄],[2] the ex-
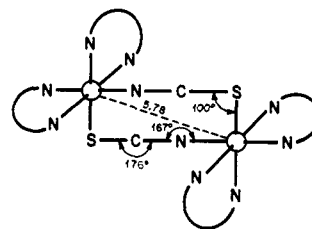
Figure 1. Schematic illustration of the structure of [Ni₂(en)₄-(SCN)₂]I₂.

change interaction takes place between two metal atoms linked by monatomic bridges and separated by ~3 Å. In the present communication we report the remarkable finding of ferromagnetic coupling, with an exchange integral $J = 5$ cm⁻¹, between two Ni atoms in di-μ-thiocyanato-tetrakis(ethylenediamine)dinickel(II) iodide. The two Ni atoms are separated by 5.8 Å and are linked by two three-atom covalent bridges (NCS⁻),[3] as illustrated schematically in Figure 1. Not only is this result unique for cluster complexes, but we believe that it is also novel for lattice ferromagnets. The closest analogy we are aware of for the latter class of compounds is the ferromagnetic interlayer interactions in CrBr₃,[4] and the intermolecular interactions in bis-(N,N-diethyldithiocarbamato)iron(III) chloride.[5] The former act *via* two intervening Br⁻ ions over a distance of 7.05 Å, but the coupling parameters are only ~0.08 cm⁻¹, two orders of magnitude smaller than the effect we report here. The latter act between iron atoms about 7 Å apart over the path Fe—S⋯S—Fe with $J \sim 0.5°$.

[Ni₂(en)₄(SCN)₂]I₂ was prepared[6] by crystallization from an aqueous ethanolic solution (50% v/v) containing equimolar amounts of [Ni(en)₂(SCN)₂] and NaI. The product was twice crystallized from aqueous ethanol and found to analyze correctly. Magnetic susceptibility measurements were made between 1.5 and 300°K with a null-coil pendulum magnetometer[7] on three different samples contained in gelatin capsules. A magnetization curve determined at 1.65°K over the range 1–15.3 kOe showed the susceptibility to be field independent. A typical set of results is shown in Figure 2 in the form of plots of $\mu_{eff} = 2.8273(\chi_A'T)$ and $1/\chi_A'$. χ_A' is the susceptibility per gram atom of Ni and includes a diamagnetic correction[8] ($\chi_d = -157 \times 10^{-6}$ cm³ g atom⁻¹). The estimated uncertainty in μ_{eff}, indicated by the error bars in the figure, is ±0.05 BM.

At 292°K, $\mu_{eff} = 3.04$ BM. As the temperature is decreased, μ_{eff} gradually increases until a maximum value of ~3.3 BM is reached at ~20°K. Below 7°K, μ_{eff} decreases rapidly, reaching 2.37 BM at 1.65°K. An $S' = 2$ state of a nickel dimer, in which all four e_g

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