may enhance HCN production to significant concentrations (*24*). In view of the toxicity (*25*) of HCN, the determination of HCN in catalytically treated automotive exhaust is recommended. A much more comprehensive analysis of the effects of catalytic exhaust treatment than heretofore reported is warranted, since other potentially hazardous compounds may be found. For instance, in the present study, in addition to HCN, COS and $(CH_3)_2NH$ were tentatively identified (by GC) as components of dry reactor effluents.

R. J. H. VOORHOEVE
Bell Laboratories,
Murray Hill, New Jersey 07974
C. K. N. PATEL
Bell Laboratories,
Murray Hill and *Holmdel, New Jersey*
L. E. TRIMBLE
R. J. KERL
Bell Laboratories, Murray Hill

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7. A paper detailing the results of kinetic and thermal desorption data for Pt and other catalysts will be published elsewhere (R. J. H. Voorhoeve, C. K. N. Patel, L. E. Trimble, R. J. Kerl, P. K. Gallagher, J. P. Remeika, in preparation).
8. The honeycomb catalyst was a PTX-3 catalyst obtained from Engelhard Industries, Newark, N.J. The Pt sponge was from the same source.
9. The H_2 chemisorption measurement was made by E. Vogel with a Micromeritics model 2100D Orr surface area analyzer, following the method of C. R. Adams, H. A. Benesi, R. M. Curtis, and R. G. Meisenheimer [*J. Catal.* **1**, 336 (1962)]. The N_2 adsorption was measured by F. Schrey with a Perkin-Elmer Sorptometer.
10. The HCN in He was obtained from Scientific Gas Products, Inc. Lots with analyses of 1040 and 1010 ppm, respectively, were used. The analysis was carried out according to the wet chemical method of M. B. Jacobs [*Analytical Chemistry of Industrial Poisons, Hazards and Solvents* (Interscience, New York, 1949), pp. 451–457]; accuracy, ± 2 percent of component.
11. Measurements were made at Gollub Analytical Service, Berkeley Heights, N.J.
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17. A preliminary theoretical search based on the only available high-precision determination of the $2\nu_2$ HCN vibrational-rotational frequencies by Brim *et al.* (*13*) indicated additional coincidence between (i) the $P_{25-24}(10)$ CO laser line at 1472.91 cm^{-1} and the HCN $2\nu_2$ R(19) line at 1472.97 cm^{-1} and (ii) the $P_{24-23}(7)$ CO laser line at 1506.99 cm^{-1} and the HCN $2\nu_2$ R(30) line at 1506.98 cm^{-1}. This could not be confirmed experimentally, however.
18. For the experiments reported here the absolute values of HCN concentrations obtained from the IR measurements have error limits of ± [(5 percent of the quoted HCN concentration) ± 5 ppm]. Plans are under way to improve these limits significantly. Further experimental details of this measurement technique will be published elsewhere (C. K. N. Patel and R. J. Kerl, in preparation).
19. In the presence of H_2O, the water gas shift reaction $CO + H_2O = CO_2 + H_2$ converts about 34 percent of the CO at 710°C. In the presence of SO_2, the shift reaction is largely inhibited.
20. The effect of H_2O may be due to hydrolysis of a NCO intermediate. The inhibition by SO_2 is understandable on the basis of the negative effects of S on the hydrogenation activity of Pt. However, these are speculations, since the mechanism of the formation of HCN is not known.
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22. After completion of this work, we found that the formation of HCN at a concentration of 1 to 15 ppm in automotive engines has been reported by M. Kaneko [*J. Jpn. Soc. Air Pollut.* **8**, 327 (1973); *Air Pollut. Abstr.* **5**, 22 (Sept. 1974)] and by R. W. Hurn, J. R. Allsup, and F. Cox [*Rep. Environ. Prot. Agency 650/2-75-014* (Dec. 1974)]. The reports by Kaneko indicate that the use of a catalytic converter diminishes the HCN emissions. Kaneko's work was done under oxidizing conditions, whereas our report deals with HCN formation in reducing conditions. We thank J. G. Cohn and K. Aykan (Engelhard Industries, Menlo Park, N.J.) for pointing out Kaneko's work to us and R. L. Bradow (Environmental Protection Agency, Research Triangle Park, N.C.) for the reference to the paper by Hurn *et al.*
23. This could happen during the transient conditions mentioned before and also if Pt were used in a "rich" mixture, for example, for the proposed use of Pt as an oxygen scavenger for a reducing Cu-Ni-Cr catalyst [see (*6*), p. 41]; temperatures of 600° to 800°C are within the normal operating range for both oxidation and reduction catalysts [see (*6*), pp. 39–41].
24. We have at present no data regarding the question of whether HCN is produced over other noble metal catalysts and, if so, whether that production is similarly suppressed by SO_2. Removal of S from gasoline has been proposed as a method of eliminating H_2SO_4 emissions caused by Pt catalysts.
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26. We thank C. A. Lambert for her help with the use of the computer; P. K. Gallagher, E. Vogel, and F. Schrey for determinations of surface areas by N_2 and H_2 adsorption; and J. P. Remeika for helpful discussions.

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The Cation $H_{13}O_6^+$: A Short, Symmetric Hydrogen Bond

Abstract. *The $H_{13}O_6^+$ ion has been found to exist as a discrete entity, forming when the cage compound $[(C_9H_{18})_3(NH)_2Cl]^+Cl$ is crystallized from hydrochloric acid solution. The aquo-cation $H_{13}O_6^+$ has crystallographic symmetry 2/m (C_{2h}). The central bond O··H··O is symmetric, with a length of 2.39 ± 0.02 angstroms; the four outer hydrogen bonds are asymmetric, with a length of 2.52 ± 0.01 angstroms. The cage compound consists of a chloride ion encapsulated within a triply bridged diammonium species, with hydrogen bond distances N(H)··Cl of 3.10 ± 0.01 angstroms.*

As a serendipitous by-product of an investigation of the crystal structure of an interesting cage compound, we have identified and determined the structure of an unusual cationic species, $H_{13}O_6^+$, consisting of a cluster of six water molecules plus an additional H^+ ion.

The cage compound that we were investigating has been named "chloridekatapinato-*in*,*in*-1,11-diazabicyclo[9.9.9]nonacosanebis(ammonium)chloride"; it has the empirical formula $[(C_9H_{18})_3(NH)_2Cl]^+Cl^-$, and forms when a chloride ion is encapsulated within the "*in*,*in*-1,11-diazabicyclo[9.9.9]nonacosanebisammonium" ion (*1*). The compound was obtained from Drs. C. Park and H. E. Simmons (Central Research and Development Department, E. I. du Pont de Nemours & Company, Wilmington, Delaware). When recrystallized from a 10 percent solution of HCl in water, it forms orthorhombic crystals, space group *Cmcm*, with unit cell dimensions a = 15.73 Å, b = 9.46 Å, and c = 24.91 Å; the unit cell contains four $[(C_9H_{18})_3(NH)_2Cl]^+$ ions, four $H_{13}O_6^+$ ions, and eight Cl^- ions. X-ray diffraction data were collected by θ-2θ scans (θ is the diffraction angle) to a maximum 2θ value of 100° (CuKα radiation). The crystal was sealed inside a thin-walled glass capillary containing a water-saturated atmosphere. The structure was derived from Patterson and electron density maps and refined by full-matrix least squares to an R index

$$R = \frac{\Sigma||F_{\text{obs.}}| - |F_{\text{calc.}}||}{\Sigma|F_{\text{obs.}}|}$$

(where $F_{\text{obs.}}$ and $F_{\text{calc.}}$ are, respectively, the observed and calculated structure factors) of 0.086 for the 524 reflections having intensities greater than 3 standard deviations (σ) above background, an R index of 0.123 for the 879 reflections having positive net intensities, and a goodness of fit

$$\left(\frac{\Sigma\left[\frac{F_{\text{obs.}}{}^2 - F_{\text{calc.}}{}^2}{\sigma\ (F_{\text{obs.}}{}^2)}\right]^2}{(n-p)}\right)$$

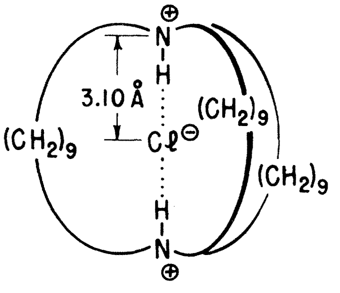

Fig. 1. The $[(C_9H_{18})_3(NH)_2Cl]^+$ ion.

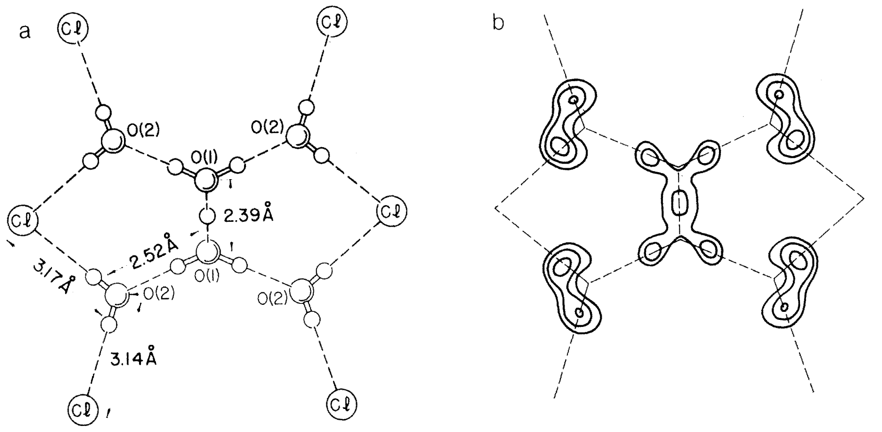

Fig. 2. (a) The $H_{13}O_6^+$ ion and the surrounding Cl^- ions. (b) Portions of a difference map, showing the electron density associated with the hydrogen atoms. Contours are drawn at 0.2, 0.3, and 0.4 electron/$Å^3$.

of 5.2 for $n = 951$ reflections measured and $p = 88$ parameters adjusted.

The rather high values of the agreement indexes reflect primarily our inability to obtain satisfactory representations of the C_9H_{18} groups, which are severely disordered. The $[(C_9H_{18})_3(NH)_2Cl]^+$ cation (Fig. 1) somewhat resembles three "C" clamps attached to a single object—the encapsulated Cl^- ion. It has the crystallographic symmetry *mm*2 (C_{2v}), one of the mirror planes passing through one of the clamps and the other lying perpendicular to them. However, for one of the $(CH_2)_9$ "clamping" groups to lie on a mirror plane, the conformations about two of the C–C bonds would have to be eclipsed, which would lead to rather severe H··H repulsions. Moreover, Fourier maps show regions of considerable electron density on both sides of the mirror plane, indicating that the symmetry results from a disorder involving a number of different, nonplanar conformations of the chain. The disorder is apparently very complicated, involving a large number of conformations. The model on which we finally settled requires twofold disorder for four of the chain carbon atoms and large, anisotropic thermal parameters for three others; even so, a difference map indicated residual electron density ranging up to 0.55 electron/$Å^3$ in some regions of this chain. The other two $(CH_2)_9$ chains were less troublesome, and we were able to obtain a fairly reasonable fit by assuming disorder for only two of the atoms in each chain.

The protonated water cluster $H_{13}O_6^+$ has crystallographic symmetry $2/m(C_{2h})$, with the central O··H··O hydrogen bond lying across a center of symmetry (Fig. 2a). The O··O distance, 2.39 ± 0.02 Å, is among the shortest such distances yet observed. It would be expected to correspond to a symmetric hydrogen bond, with the hydrogen atom located midway between the two oxygen atoms and with its potential function represented by a curve with a single minimum. A difference electron density map (Fig. 2b) supports this model; however, it cannot rule out the alternative that the hydrogen atom is disordered over two sites slightly displaced to either side of the symmetry center, and hence is better represented by a double-minimum function. As Hamilton and Ibers (*2*) have pointed out, "Clearly it is always possible to propose a degree of asymmetry that will be undetectable." But such a proposal serves little practical purpose; and in view of the extremely short O··O distance and the identical environments (due to crystallographic symmetry) of the two O(1) atoms, we believe that this cluster should be added to the list of examples of symmetric hydrogen bonds.

The O(1)··O(2) distance of 2.52 ± 0.01 Å also represents a very short hydrogen bond, but our difference map (Fig. 2b) clearly indicates that it is asymmetric, with the hydrogen atom covalently bonded to O(1). The angles at O(1) are O(1)··O(1)··O(2), 111°, and O(2)··O(1)··O(2), 132°. The O(2)–H··Cl^- hydrogen bonds are of normal length; however, they are undoubtedly vital to the stability of the $H_{13}O_6^+$ ion.

The $H_{13}O_6^+$ ion represents the largest protonated cluster of water molecules yet characterized. Examples of smaller clusters include $H_9O_4^+$ (*3*), where a central oxygen atom is surrounded by three other oxygen atoms at distances of 2.50, 2.59, and 2.59 Å; $H_7O_3^+$ (*3, 4*), a nonlinear array $H_2O··H_3O··H_2O$ with O··O distances ranging from 2.47 to 2.54 Å; and $H_5O_2^+$, which has been observed in a variety of crystals (*5*) with O··O distances ranging from 2.41 to 2.57 Å.

ROBERT A. BELL, GARY G. CHRISTOPH
FRANK R. FRONCZEK, RICHARD E. MARSH
Department of Chemistry, A. A. Noyes
Laboratory of Chemical Physics,
California Institute of Technology,
Pasadena 91125

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Hyperbaric Hydrogen Therapy: A Possible Treatment for Cancer

Abstract. *Hairless albino mice with squamous cell carcinoma were exposed to a mixture of 2.5 percent oxygen and 97.5 percent hydrogen at a total pressure of 8 atmospheres for periods up to 2 weeks in order to see if a free radical decay catalyzer, such as hydrogen, would cause a regression of the skin tumors. Marked regression of the tumors was found, leading to the possibility that hyperbaric hydrogen therapy might also prove to be of significance in the treatment of other types of cancer.*

Over a period of years Dole and his collaborators (*1*) have studied the radiation chemistry of polyethylene (PE) and discovered a pronounced catalytic effect of molecular hydrogen in catalyzing the decay of the alkyl radicals, $-CH_2\dot{C}HCH_2-$ in the solid PE at room temperature. For example, Waterman and Dole (*2*) found that at 24°C an ambient hydrogen pressure of 400 torr increased the first order decay constant of the alkyl radical by about tenfold. Furthermore, the catalytic effect was the result of the hydrogen dissolved in the PE. Wen, Johnson, and Dole (*3*) showed that the tenfold increased catalytic activity of hydrogen at 600 torr in single crystalline mats of PE as compared to that in bulk PE was the result of a tenfold greater solubility of hydrogen in the single crystalline PE.

Free radicals have been thought to be involved in cancerous growths (*4*); we now report the effect of hydrogen gas on cancer (*5*). We chose as experimental animals hairless albino mice on whose skin