The structure of 2 and the reactions of 1 and 2 are under investigation.

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The Formation of CB₅H₉ and Its 1-Methyl Derivative from 1,7-C₂B₆H₈

Sir:

We wish to report the preparation of the parent member of the CB_nH_{n+4} carborane series, where $n = 5$, 2-carbahexaborane(9), CB_5H_9,[1] and its 1-methyl derivative, both of which have not been previously reported, although several alkyl derivatives are known.[1-3]

The reaction between 1,7-dicarba-*closo*-octaborane-(8), $C_2B_6H_8$,[4-6] and tetramethylammonium borohydride[7] in diglyme at 100° for 24 hr yields as yet uncharacterized ionic products. Removal of the solvent by vacuum distillation followed by heating at 85° *in vacuo* for 10 hr produced a solvent-free solid. The solid was then treated with an excess of dry HCl, and a mixture of neutral compounds was liberated and separated using standard vpc methods. Three major fractions were collected and characterized.

The mass spectrum of 2-carbahexaborane(9), CB_5H_9 (Figure 1), the major fraction formed in approximately 20% yield, exhibited a cutoff at m/e 76 which corresponds to the $^{12}C^{11}B_5{}^1H_9{}^+$ ion. The 60-Mc/sec ^1H nmr spectrum consisted of a broad peak at τ 4.62 relative to internal tetramethylsilane (TMS). The ^{11}B nmr spectrum (Figure 1) consisted of three sets of doublets of relative area 2:2:1 which is consistent with a species containing five borons in a pentagonal pyramid structure. The doublet at lowest field shows secondary splitting due to bridge hydrogen coupling.

The mass spectrum of 1-methyl-2-carbahexaborane(9), 1-CH₃CB₅H₈, exhibited a cutoff at m/e 90 which corresponds to the $^{12}C_2{}^{11}B_5{}^1H_{11}{}^+$ ion. The 60-Mc/sec ^1H nmr spectrum consisted of a broad peak of relative area 3 at τ 10.58 and a broad peak of relative area 1 at τ 4.45 relative to internal TMS. The ^{11}B nmr spectrum (Figure 1) consisted of two sets of doublets and a singlet of relative area 2:2:1, respectively. The high-field singlet indicates substitution at the 1 position.

The third fraction identified from the reaction was 3-methyl-2-carbahexaborane(9), 3-CH₃CB₅H₈, which was identical with that reported earlier.[1]

(1) T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **88**, 2061 (1966).
(2) R. N. Grimes and C. L. Bramlett, *ibid.*, **89**, 2557 (1967).
(3) M. A. Grassberger, E. G. Hoffman, G. Schomburg, and R. Köster, *ibid.*, **90**, 56 (1968).
(4) R. E. Williams and F. J. Gerhart, *ibid.*, **87**, 3513 (1965).
(5) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **90**, 869 (1968).
(6) G. B. Dunks and M. F. Hawthorne, *Inorg. Chem.*, **7**, 1038 (1968).
(7) Sodium borohydride gives similar results; however, the ionic species formed is difficult to separate from residual solvent.
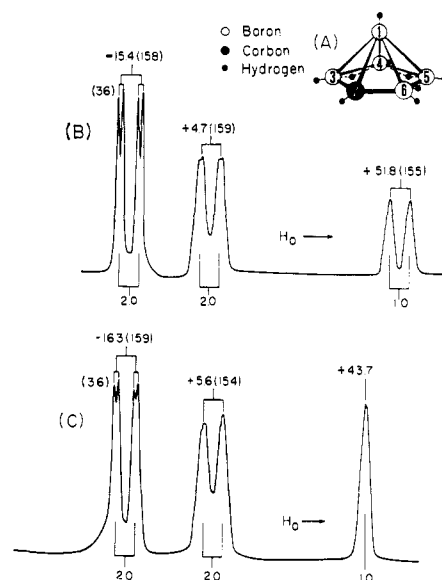
Figure 1. (A) The molecular structure of 2-carbahexaborane(9), CB_5H_9. The 32.1-Mc/sec ^{11}B nmr spectra of CB_5H_9 (B) and 1-$CH_3CB_5H_8$ (C). Chemical shifts (ppm, relative to $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (cps) are indicated. Relative areas appear beneath the peaks.

Even though the removal of boron atoms from carborane cages is well known both by pyrolytic and chemical methods,[6,8-13] this appears to be the first example of the removal of cage carbon atoms from a closed carborane.

The characterization of the ionic species and several minor components also obtained in this reaction, together with the results of the reaction between C-methyl and C,C′-dimethyl-1,7-dicarba-*closo*-octaborane(8) with borohydride ion, will be presented elsewhere.

Acknowledgment. This research was supported in part by the Office of Naval Research.

(8) T. P. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).
(9) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 607 (1966).
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(12) M. F. Hawthorne and A. D. Pitts, *ibid.*, **89**, 7115 (1967).
(13) J. N. Francis and M. F. Hawthorne, *ibid.*, **90**, 1663 (1968).

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The Nuclear Overhauser Enhancement of the Carbon-13 Magnetic Resonance Spectrum of Formic Acid

Sir:

The difficulties associated with detecting the carbon-13 isotope in its 1.1% natural abundance are well known, and therefore it is important to characterize the dramatic improvement in the ratio of signal to noise realized with proton decoupling methods. In addition to the enhancement expected from proton multiplet collapse, application of a proton decoupling radio-
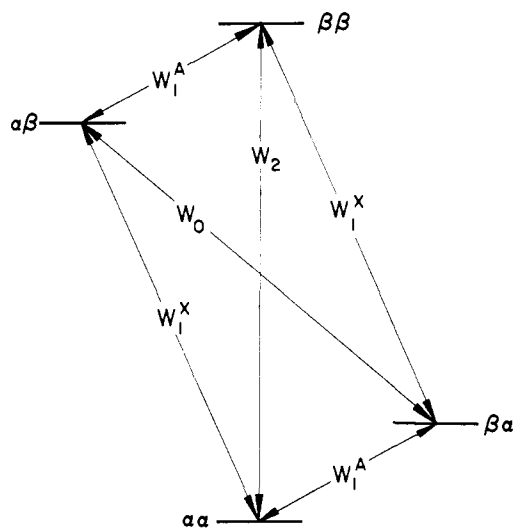
Figure 1. The transition probabilities governing the relaxation process are specified in terms of the four energy levels characteristic of the AX spectral system. The subscripts on the W's indicate the quantum change in the angular momenta while the superscripts identify the nucleus undergoing a transition for the unit change in spin.
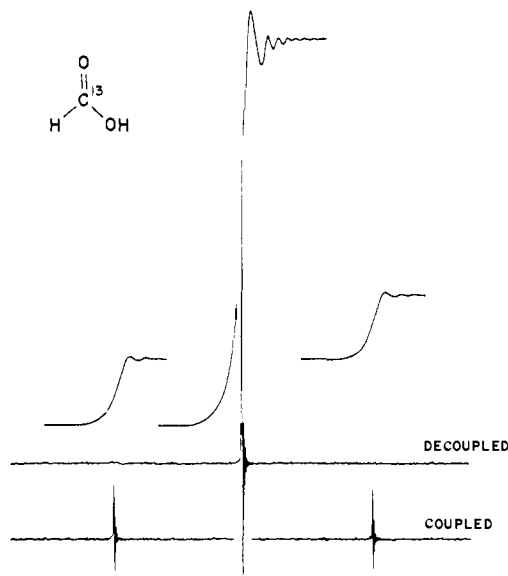

Figure 2. The coupled and decoupled carbon-13 spectra of 23% enriched formic acid exhibit a 2.98 nuclear Overhauser enhancement in peak heights and integrated intensities. The integrals, obtained at slower sweep rates and at expanded sweep widths, were used to quantitatively measure this factor.

frequency field further enhances the signal intensity by several fold through a nuclear Overhauser effect. This communication reports the magnitude of this latter enhancement factor in formic acid, and from theoretical considerations of the proton–carbon-13 dipole–dipole relaxation mechanism certain conclusions are drawn regarding the dominant relaxation mechanism for the carbon-13 isotope.

Solomon[1] has shown for an AX system of two spins $1/2$, such as found in formic acid (HCO_2H),[2] that the ratio of the magnetic polarization of the A spin with and without a strong decoupling field centered at the resonance of X is given by

$$\frac{\langle Mz^A \rangle}{\langle Mz^A \rangle_0} = 1 + \frac{W_2 - W_0}{2W_1^A + W_2 + W_0}\left(\frac{\gamma_X}{\gamma_A}\right) \quad (1)$$

This expression, which may be derived using a steady-state approximation, depends on the relaxation mechanisms affecting nucleus A through the transition probabilities W_0, W_1^A, and W_2 and on the ratio of the two gyromagnetic constants, γ_X/γ_A, which is 3.976 when X is hydrogen and A is carbon-13. Figure 1 defines the various W's in terms of the four energy levels which characterize the AX spin system. It is well to note that the enhancement is independent of the rate of relaxation, W_1^X, of the X nucleus providing saturation of the two X transitions is achieved. This condition is easily realized in the formic acid system as saturation always accompanies the elimination of the proton splitting in the carbon-13 resonance.

In the absence of any other relaxation process, the dipole–dipole coupling mechanism gives rise to the following relationships[1] between the W's.

$$W_2 : W_1^A : W_0 = 1 : 1/4 : 1/6 \quad (2)$$

Substitution of these values for the W's along with the value for γ_X/γ_A into eq 1 yields a theoretical estimate of

(1) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).
(2) The acidic proton in formic acid does not induce splittings in either the A or X nuclei due to rapid chemical exchange.

2.988 for the nuclear Overhauser enhancement factor. Introduction of other relaxation mechanisms into the carbon-13 relaxation process can only increase the W_1^A term in eq 1, and such a change will reduce the enhancement factor. In the limit as W_1^A becomes much greater than either W_0 or W_2, the enhancement factor can be expected to drop to unity.

The extent of enhancement was determined experimentally for a sample of formic acid 23% enriched in carbon-13 by observing and integrating the spectrum with and without decoupling. The enriched sample facilitated integration techniques allowing the enhancement ratio to be determined with a reproducibility which is better than 5%. Figure 2 compares the coupled and decoupled carbon-13 spectra of formic acid obtained on a Varian AFS-60 spectrometer. Incoherent random noise decoupling[3] was used in this instance, but similar results also can be obtained with ordinary coherent strong field decoupling. The integrals shown were obtained at slower sweep rates and at expanded sweep widths from four accumulated scans in a Varian C-1024 time-averaging device. The mean of three such measurements gives an enhancement factor of 2.98 ± 0.15 which agrees exceptionally well with the 2.988 factor obtained by assuming the dipolar mechanism to be dominant. On this basis all other relaxation mechanisms, which would decrease the theoretical estimate, are assumed to be negligible for formic acid.

Since the effectiveness of the proton–carbon-13 dipole–dipole mechanism depends upon the C–H separation as $1/r_{CH}^6$, directly bonded protons are of overwhelming importance in establishing the magnitude of this relaxation term. Because of the sixth-order distance attenuation of the dipolar mechanism in carbons with no directly bonded protons, other mechanisms can be expected to be competitive with the dipolar term and thereby decrease the nuclear Overhauser enhancement factor. This is probably the best

(3) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

explanation for the low peak intensities recorded[4] for bridgehead carbons in polycyclic aromatics. This is especially noticeable for C-15,16 in pyrene.

A generalized treatment[5] of more complicated spin systems indicates that an enhancement factor of 2.988 can also be expected for CH_2 and CH_3 systems providing assumptions similar to those used in the derivation of eq 1 are invoked and providing other relaxation mechanisms continue to remain small.

The success of proton decoupling methods as a way for making carbon-13 radiofrequency spectroscopy feasible for routine studies depends in a large measure upon the nuclear Overhauser enhancement factor which has been shown herein to have a rather sizable magnitude. It is understandable therefore that random noise decoupling methods[3] presently being used in this and other[6] laboratories should constitute a significant development in the detection of the carbon-13 isotope in its 1.1% natural abundance.

(4) T. D. Alger, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **88**, 5397 (1966).

(5) K. F. Kuhlmann and D. M. Grant, manuscript in preparation.

(6) Private communications from J. D. Roberts and F. J. Weigert (California Institute of Technology) and from R. Johnson (Varian Associates).

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A New Metal Cluster System Containing a Cube of Metal Atoms

Sir:

In recent years metal atom cluster compounds have received considerable study,[1] especially since the bonding in these compounds[2] generally suggests significant metal–metal interaction. To date three symmetrical metal atom cluster arrangements have been observed.[3] These include (1) the triangular trinuclear clusters, *e.g.*, $Re_3Cl_{12}^{3-}$ or $Os_3(CO)_{12}$; (2) the tetrahedral tetranuclear clusters, *e.g.*, $Co_4(CO)_{12}$ or Cu_4L_4,[4] where $L = S_2CN(C_2H_5)_2$; and (3) the octahedral hexanuclear clusters,[2,3] *e.g.*, $[Nb_6Cl_{12}]^{2+}$ or $[Mo_6Cl_8]^{4+}$. In this paper we present the first structural evidence for a fourth class containing a *cubic* octanuclear cluster of metal atoms. The compound which displays this configuration is the phenyltrimethylammonium salt of $[Cu_8(i\text{-}MNT)_6]^{4-}$ where i-MNT is 1,1-dicyanoethylene-2,2-dithiol, $S_2CC(CN)_2^{2-}$.

The preparation and characterization of the tetrapropylammonium and tetraphenylarsonium salts of

(1) F. A. Cotton, *Quart. Rev.* (London), **20**, 389 (1966); J. Lewis, *Pure Appl. Chem.*, **10**, 11 (1965).

(2) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

(3) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 656.

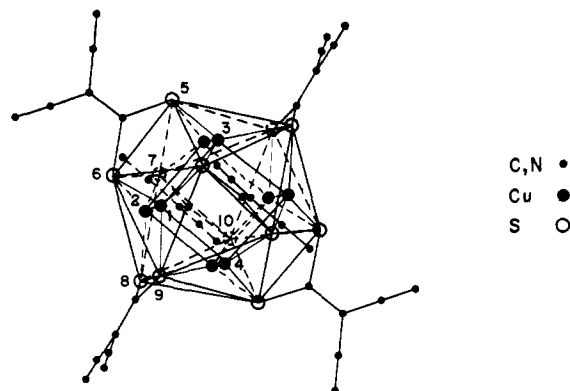(4) R. Hesse, *Arkiv Kemi*, **20**, 481 (1962).

Figure 1. A projection of the $Cu_8(i\text{-}MNT)_6^{4-}$ anion down the *b* axis of the unit cell.

$[Cu_8(i\text{-}MNT)_6]^{4-}$ have been reported.[5] Based on the observation of a single sharp CN stretch in the infrared spectrum, the diamagnetism of the solid, a conductivity measurement in nitromethane,[6] and the known tetrahedral structure of copper(I) atom clusters, the tetrahedral arrangement was postulated. In this structure, the sulfur atoms were placed at the edges of the tetrahedron, thus making the CN groups nearly (but not exactly) equivalent.

The crystal structure of the phenyltrimethylammonium salt of $[Cu_8(i\text{-}MNT)_6]^{4-}$ was found to have Laue symmetry 2/m with lattice constants $a = 15.49$ Å, $b = 15.71$ Å, $c = 20.76$ Å, and $\beta = 132° 36'$. Monoclinic space group $P2_1/c$ was indicated by systematic absences of the types $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$. The density, 1.684 g/cm³, as determined by flotation, is consistent with the calculated value of 1.688 g/cm³, with two molecules per unit cell.

Intensity data were taken on a Picker four-circle goniostat using Ni-filtered, Cu radiation (λ 1.5418 Å). These intensities were then corrected for absorption, Lorentz, and polarization effects. The data were placed on an absolute scale using a Wilson plot and an E-map constructed using 416 signed coefficients as determined by symbolic addition.[7] The E-map revealed the locations of four copper atoms in the asymmetric unit, and these, used as an initial model, provided sufficient phasing for the complete structure determination by means of iterative Fourier and least-squares[8] refinement.

An intermediate model including positional parameters and isotropic temperature factors for the 48 nonhydrogen atoms of the asymmetric unit, together with the real and imaginary dispersion corrections for copper and sulfur, has been refined by full-matrix least squares. The crystallographic R factor for this model, using all 2968 observed structure factors, is 0.068. The two phenyltrimethylammonium cations of the asymmetric unit included in this refinement have

(5) J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

(6) The conductivity reported[5] was based on a molecular weight assumption which is incorrect. A recalculation using the correct molecular weight gives a Λ (10^{-3} M) of 259 ohm^{-1} M^{-1}, a reasonable value for a 4:1 electrolyte.

(7) R. Dewar and A. Stone, FAME-MAGIC-LINK-SIMPL, University of Chicago, Chicago, Ill.

(8) W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS and ORFFE, Oak Ridge National Laboratory, Oak Ridge, Tenn.