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.

Acknowledgments. We are indebted to Professor E. G. Paul (Brigham Young University) for the preparation of the enriched formic acid sample. This work was supported by the Public Health Service under Grant GM 0-8521-8 awarded by the National Institutes of Health.

(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 $[Cu_8(i\text{-MNT})_6]^{4-}$ 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.

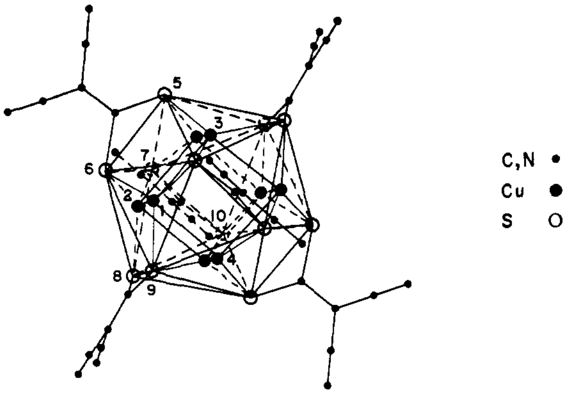

Figure 1. A projection of the $Cu_8(i\text{-MNT})_6{}^{4-}$ anion down the *b* axis of the unit cell.

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

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(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).

(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.

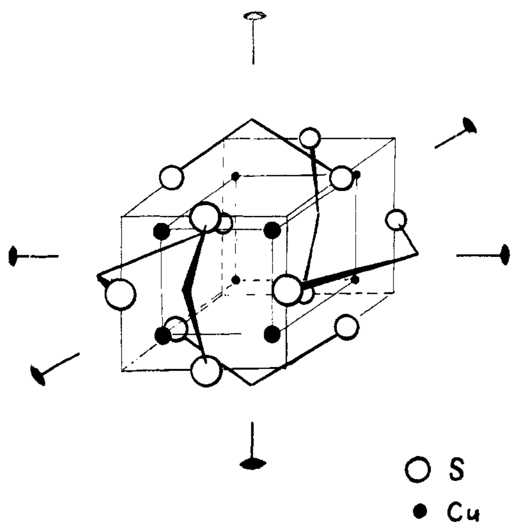

Figure 2. A schematic picture of the cluster.

normal structures. Further detailed refinement is in progress.

The molecular structure of the Cu$_8$(i-MNT)$_6^{4-}$ anion is shown in Figure 1. Selected geometrical data for this structure are presented in the table. The complex consists of a slightly distorted cube of copper atoms embedded within the cluster of 12 sulfur atoms which lie on the vertices of a systematically distorted icosahedron. This group of 20 atoms is enclosed by six $^-$CS$_2$ carbon atoms located at the vertices of an octahedron. The distortions mentioned are of the following form: (a) the three longest Cu–Cu distances listed in the table are all associated with Cu-4, indicating that the distortion is principally rhombohedral; (b) 6 of the 30 edges of the sulfur icosahedron are shorter than the other 24 (3.08 *vs.* 3.87 Å). These six edges are the sulfur–sulfur "bite" distances of the six ligands. While the crystallographically required point symmetry of the 56-atom anion is C$_i$, the idealized point symmetry is T$_h$.[9]

Table I. Some Interatomic Distances in the Cu$_8$(i-MNT)$_6^{4-}$ Anion[a]

Bond distances, Å			Sulfur–sulfur distances, Å		
	Atoms			Atoms	
Cu–Cu	1–2	2.811	S–S "bite"	5–6	3.079
	1–3	2.806		8–9	3.088
	1–4	2.865		7–10	3.077
	2–3 (1)[b]	2.783	S's coordinating metal atom indicated		
	2–4 (1)	2.871			
	4–3 (1)	2.832	Cu-2	6–7	3.818
				7–8	3.871
Cu–S	1–6	2.241		8–6	3.877
	1–9	2.237	Cu-1	6–9	3.855
	1–10 (1)	2.258		9–10 (1)	3.863
	2–6	2.249		10 (1)–6	3.880
	2–7	2.252	Cu-3	5–10 (1)	3.921
	2–8	2.238		10 (1)–8 (1)	3.874
	3–5	2.266		8 (1)–5	3.856
	3–8 (1)	2.262	Cu-4 (1)	5–7	3.857
	3–10 (1)	2.257		7–9 (1)	3.871
	4–5 (1)	2.249		9 (1)–5	3.914
	4–7 (1)	2.249			
	4–9	2.256			

[a] Standard errors of these distances from ORFFE[8] are: Cu–Cu 0.003 Å, Cu–S 0.004–5 Å, S–S 0.005–7 Å. [b] The (1) indicates the atom related by the symmetry center to the one numbered.

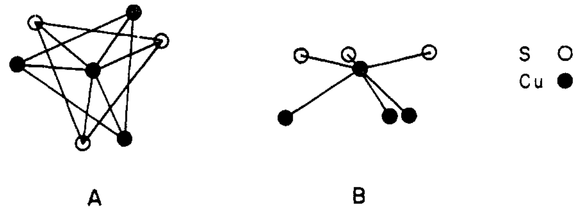

Figure 3. Views of the coordination about the copper atoms in Cu$_8$(i-MNT)$_6^{4-}$ (A) parallel to a threefold axis and (B) perpendicular to a threefold axis.

A schematic description of the structure of the anion is presented in Figure 2. Here the small cube of copper atoms, ~3 Å on an edge, is pictured as surrounded by a larger cube ~4 Å on edge, with sulfur atoms at edge centers. The relatively short "bite" S–S distance forces a distortion of this larger cube, however, so that if the structure is viewed down a threefold axis (Figure 3A) the first equilateral triangle of sulfur atoms appears rotated ~30° from superposition on the first equilateral triangle of copper atoms. Each chelate ligand is closely associated with four copper(I) atoms with each sulfur atom bonded to two of the four copper atoms.

The average Cu–Cu distance in the cluster is 2.83 Å, a distance 0.1–0.2 Å larger than the Cu–Cu distance in tetrahedral copper(I) clusters[1,4] and ~0.3 Å larger than this distance in the metal.

If one assumes that each sulfur atom contributes four electrons to the bonding in the Cu$_8$ cluster and each copper(I) ten electrons, the 128 electrons leave the system 16 electrons short of achieving a closed-shell noble gas configuration, or two electrons per copper atom. Thus a valence-bond description would require two of the three Cu–Cu nearest-neighbor interactions to be bonding about each copper(I) atom.[10] Since the sulfur atoms in i-MNT resemble a heavy halide ion in coordinating ability, it seems reasonable to believe that examples of a Cu$_8$X$_{12}^{4-}$ cluster, where X = Br$^-$ or I$^-$, should be found.

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(9) Point group O$_h$ has C$_4$, C$_3$, and C$_2$ rotational symmetry elements while point group I$_h$ (icosahedral) has C$_5$, C$_3$, and C$_2$. Point group T$_h$, with C$_3$ and C$_2$ rotation, is the highest subgroup common to O$_h$ and I$_h$. It is reasonable to assume that the Cu$_8$(i-MNT)$_6^{4-}$ cluster takes on its idealized T$_h$ symmetry in solution since there is no apparent explanation for the distortions observed except to attribute them to crystal-packing considerations. Few examples are known of molecular species with this idealized point symmetry. A referee has correctly cited the Ce(NO$_3$)$_6^{3-}$ ion in Mg$_3$Ce$_2$(NO$_3$)$_{12}\cdot$24H$_2$O (A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Chem. Phys.*, **39**, 2881 (1963)). The structures of K$_3$Co(NO$_2$)$_6$ (M. van Driel and H. J. Verweel, *Z. Krist.*, **95**, 308 (1936)) and K$_2$B$_{12}$H$_{12}$ (J. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960)) show *T*$_h$ symmetry anions in crystals but the average idealized geometry in solution is described as O$_h$ and I$_h$, respectively. The Fe(C$_5$H$_5$N)$_6^{2+}$ ion (R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 4847 (1966)) also displays an idealized T$_h$ symmetry.

(10) A detailed MO treatment along the lines of the treatment of F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964), is in progress.

Society. Thanks are also given to Mr. Anthony D'Addario for his help in the structural analysis.

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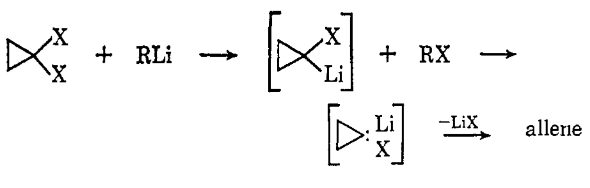
An Investigation of the Reaction between 1,1-Dichlorocyclopropanes and Alkyllithium Reagents Using Chemically Induced Dynamic Nuclear Polarization

Sir:

The reactions of *gem*-dihalocyclopropanes with alkyllithium compounds have been applied to the synthesis of allenes[1] and of strained polycyclic systems.[2] The reaction sequence, in the case of allene formation, is generally accepted to proceed first to an α-halolithium intermediate, then, perhaps, through a carbene–lithium halide complex. The intermediacy of α-halolithium compounds has been established in other *gem*-dihalide systems by trapping at low temperatures,[3] but no direct evidence is available in the *gem*-dihalocyclopropane series.



Since the formation of the α-halolithium intermediates involves a halogen–metal exchange, it seemed appropriate to search for chemically induced dynamic nuclear polarization (CIDNP), which has been found in other halogen–metal exchange reactions.[4] The CIDNP phenomenon depends on the polarization of nuclei (protons in this case) in short-lived free-radical intermediates and is observed by scanning the nmr spectrum of the reacting solution.[5] Both enhanced absorption (+ polarization) and emission (− polarization) arise from the protons of the products of free-radical reactions.

We have examined the reaction of 1,1-dichloro-2,2-dimethylcyclopropane (**1**) with ethyllithium in benzene–ether (30:1) at *ca.* 40° to give 3-methyl-1,2-butadiene (**2**) and 1-chloro-2,2-dimethylcyclopropane (**3**) as major products. Figure 1 shows the nmr spectrum[6] taken (a) before the reaction was initiated by the addition of ether,[7] (b) during the reaction, and (c) at its completion.

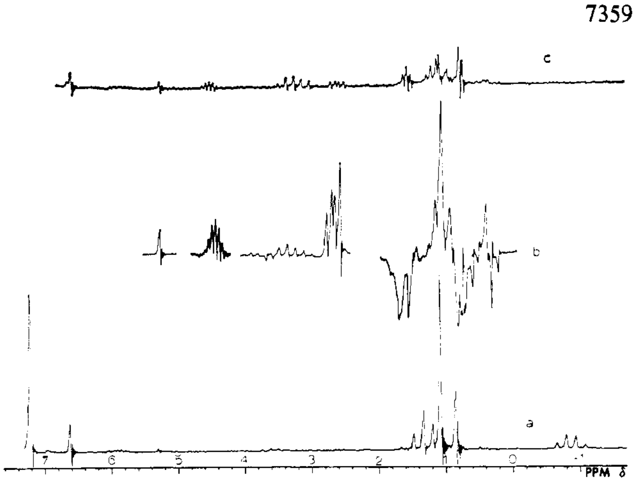


Figure 1. (a) Nmr spectrum of a solution of ethyllithium and **1** in benzene; (b) composite of several scans taken within seconds after ether has been added to initiate the reaction; (c) scan after the reaction is complete; benzene amplitude is × 0.1.

Because the maximum polarization often can be observed only for a short time compared to the time needed for a complete scan, Figure 1b is a composite of scans of different regions of the spectrum taken at the appropriate time in several reactions run under similar conditions. The effect of polarization on the protons of both of the major reaction products is observed. For the allene **2**, the vinyl protons (δ 4.45) show + polarization; the methyl protons of **2** may be polarized but do not account for all of the emission observed at δ 1.4–1.9. The proton α to the chlorine in **3** is strongly polarized (doublet of doublets at δ 2.61), and the emission and enhanced absorption at δ 0.25–0.6 match very well with an authentic absorption spectrum of **3**, although additional lines are present.

The use of emission as proof for polarization is not open to question, but lines which show only enhanced absorption must be more critically examined to exclude the possibility that the change in absorption intensity results from a rapid product formation and subsequent destruction by further reaction. If the polarization is sufficiently intense, however, its presence can be established conclusively by a comparison of the absorption intensity with the maximum intensity possible if all of the starting material were converted to the product in question. For example, the observed area of the septuplet at δ 4.45 (two protons) is twice as large as the singlet for the methylene protons in the starting material **1** (also two protons). The absorption in the same region at the end of the reaction is proper for the 44% yield of **2** as analyzed by gas chromatography.

We believe that these results are best explained by the sequence in Scheme I. Transfer of an electron from ethyllithium to **1** gives a caged radical pair which can disproportionate to give **3**, couple to give **4**, or transfer an electron either to return to **1** or proceed to the α-halolithium intermediate **5**. Proton polarization occurs in the free radicals before reaction to give diamagnetic products. Evidence for the return to **1** rests on the emission line at δ 0.85, but the identity of this line is still open to question.

The polarization at δ 2.61 is unique, comprising the first example of a nucleus which is polarized in one free

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[1] W. R. Moore and H. R. Ward, *J. Org. Chem.*, 27, 4179 (1962); L. Skattebøl, *Tetrahedron Letters*, 167 (1961).

[2] W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

[3] D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965).

[4] H. R. Ward, R. G. Lawler, and R. A. Cooper, submitted for publication.

[5] H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967).

[6] Spectra were taken on a Varian A-60-A at 1000-Hz sweep width. The spectrometer was purchased with funds supplied by the National Science Foundation.

[7] J. K. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171, (1963).