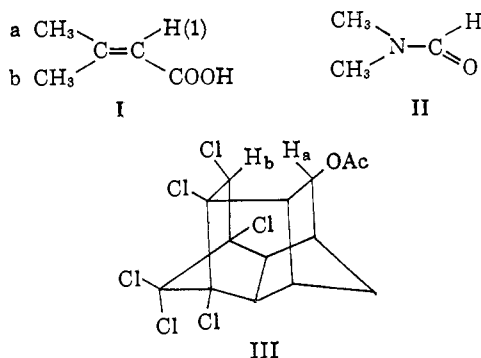


nuclei will be correspondingly reduced. Thus, it is possible to determine experimentally from NOE values which nuclei in a molecule are responsible for the relaxation of any particular nucleus. Also, since the relaxation is very strongly dependent on the distance between a pair of nuclei, studies of NOE's under the conditions described above should be of considerable stereochemical and conformational interest in organic chemistry.



As an illustration, we can take β,β -dimethylacrylic acid (I) and consider which protons are likely to contribute to the intramolecular relaxation of H(1). The carboxyl proton is not very close to H(1) since I probably exists largely as a cyclic hydrogen-bonded dimer. Of the two methyl groups, b is so much further from H(1) than is a that it should not contribute appreciably to the relaxation of H(1). Thus H(1) should be relaxed largely by the protons in a. Therefore, saturation of the protons in a should give a NOE for H(1), whereas saturation of the protons in b should do nothing to the intensity of the band of H(1). The problem is complicated by small long-range couplings of H(1) to both a and b. Complete saturation of either a or b protons can be achieved by double irradiation,⁷ but only under conditions that decoupling occurs. However, the decoupling is an extra phenomenon that does not affect integrated intensities provided that the spectrum is observed by means of a frequency sweep.⁸

The spectrum of I, as a 9% solution in benzene- d_6 , was observed by a frequency sweep⁸ method with 9% benzene in the solution as a reference line for a field-frequency lock.⁸ The methyl groups gave two well-separated doublets ($J = 1.3$ c.p.s. for both doublets); the upfield doublet (τ 8.58) can be assigned⁹ to the methyl group a and the downfield doublet (τ 8.03) to methyl group b. The band of H(1) was approximately a 1:6:15:20:15:6:1 septet (τ 4.34), owing to the virtually equal coupling to each of the methyl groups. Irradiation of either of the two methyl bands resulted in the band of H(1) changing to a 1:3:3:1 quartet, but, more important, the integrated intensity of the quartet was higher when the high-field methyl group was irradiated (relative intensity = 117 ± 1) than when the low-field methyl group was irradiated (relative intensity = 96 ± 1) or than when the irradiation frequency was offset from the methyl groups (relative intensity = 100 ± 2). Thus it is the upfield methyl group which is *cis* to H(1), in agreement with the

previous assignment⁹ based on chemical shifts. Saturation of H(1) did not result in any significant change in the intensity of either methyl group. Thus, the protons of a methyl group relax one another, and outside protons contribute little by comparison.

A similar experiment carried out on an 8% solution of dimethylformamide (II) in deuterium oxide gave the following results for the changes in integrated intensity of the formyl proton over that observed without double irradiation: $+18 \pm 1\%$ (low-field methyl saturated), $-2 \pm 1\%$ (high-field methyl saturated). Thus the low-field methyl is *cis* to the formyl hydrogen, in agreement with previous, but not entirely unambiguous, assignments.¹⁰

If a molecule has two protons which are particularly close together (*e.g.*, the half-cage acetate¹¹ (III)), then of course these two protons will relax one another very effectively. So effective is the dipolar interaction of H_a with H_b in III that an increase in the intensity of the band of either of these protons was observed when the other band was saturated, even when oxygen was not removed from the solution.

The present method seems to be of wide applicability, but care must be taken in interpreting small changes in intensities.¹² A differential effect, as observed for I and II, is unambiguous.

(10) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **32**, 1272 (1960); J. V. Hatton and R. E. Richards, *Mol. Phys.*, **5**, 139 (1962); L. A. LaPlanche and M. T. Rogers, *J. Am. Chem. Soc.*, **85**, 3728 (1963).

(11) S. G. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *ibid.*, **82**, 5377 (1960). We are indebted to Dr. Soloway for a gift of compound III. For further details of the spectrum of III, see F. A. L. Anet, A. J. R. Bourn, P. Carter, and S. Winstein, *ibid.*, **87**, 5249 (1965).

(12) Overloading of the audio phase-sensitive detector can easily occur when an intense line is irradiated, but such effects can be overcome by (a) using a more dilute sample, (b) decreasing the input to the detector, or (c) removing the unwanted frequency by filtering. In any case, spurious effects generally cause a decrease in the intensity of a band and thus cannot be confused with a NOE. The present experiments were carried out at 60 Mc.p.s. on a modified³ Varian HR 60 spectrometer.

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Received August 2, 1965

A New Type of Cyclic Transition Metal Complex, $[\text{Ni}(\text{SC}_2\text{H}_5)_2]_6$

Sir:

We wish to report the structure and stereochemistry of a nickel mercaptide hexamer which has been definitely established by a single-crystal X-ray analysis as the first representative of a new type of transition metal cluster.

Nickel mercaptides have previously been reported as *insoluble* high polymers,^{1,2} but through the use of organotin-sulfur compounds which react with metal halides to form metal mercaptides by cleavage of the Sn-S bonds,³ we have prepared in 53% yield a *soluble*, diamagnetic, purplish black crystalline product from the reaction of nickel(II) chloride and bis(ethylthio)-dimethyltin in alcohol. Molecular weight measure-

(1) K. A. Jensen, *Z. anorg. Chem.*, **252**, 227 (1944).

(2) R. G. Hayter and F. S. Humiec, *J. Inorg. Nucl. Chem.*, **26**, 807 (1964).

(3) E. W. Abel, D. B. Brady, and B. C. Crosse, *J. Organometal. Chem.*, in press.

(8) R. Freeman and D. H. Whiffen, *Proc. Phys. Soc. (London)*, **79**, 794 (1962).

(9) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1961.

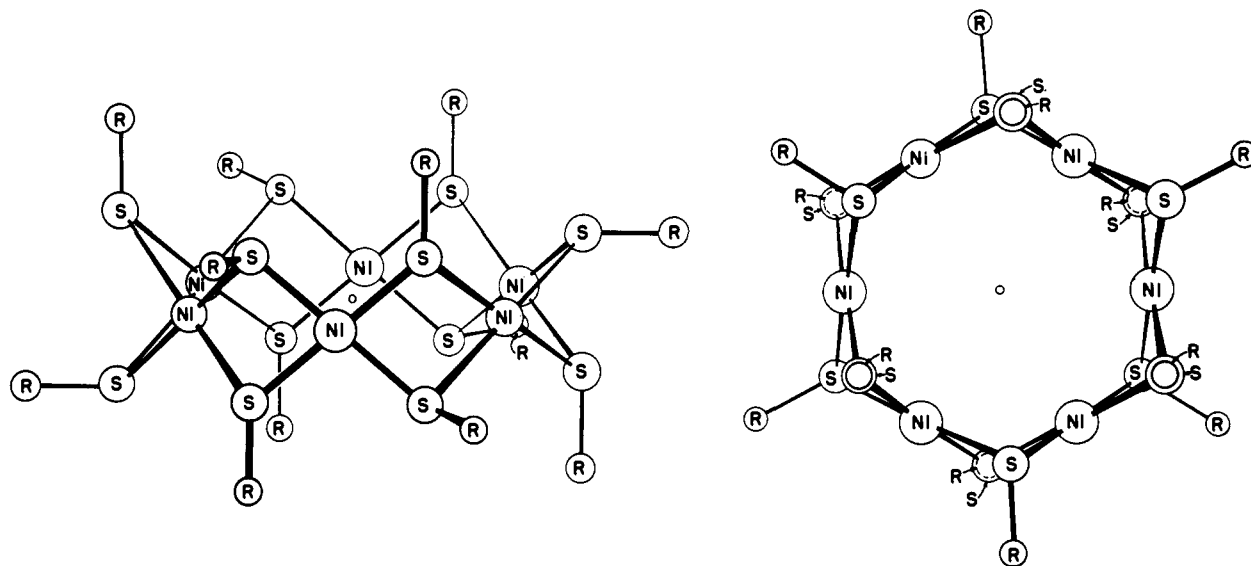


Figure 1. Molecular structure of $[\text{Ni}(\text{SC}_2\text{H}_5)_2]_6$.

ments indicated the compound of empirical formula $\text{Ni}(\text{SC}_2\text{H}_5)_2$ to exist as a hexameric species in solution. *Anal.* Calcd. for $(\text{C}_4\text{H}_{10}\text{NiS}_2)_6$: C, 26.6; H, 5.6; mol. wt., 1086. Found: C, 27.1; H, 5.6; mol. wt., 1006.⁴ This discovery prompted us to reinvestigate the reported formation² of high polymer nickel mercaptides by reaction of nickel carbonyl with dialkyl disulfides. Soluble nickel mercaptides in varying yields were produced as well as some insoluble material; for the derivatives where $\text{R} = \text{CH}_3$ or C_6H_5 (both previously reported²), the formula $[\text{Ni}(\text{SR})_2]_n$ was indicated by analysis of the insoluble material. The soluble product obtained from the reaction of diethyl disulfide with nickel carbonyl in benzene was found to be identical with the above hexameric species, yield 20%. *Anal.* Found: C, 26.3; H, 5.4; mol. wt., 1177.⁴ Recrystallization from hexane yielded tabular crystals from which (after considerable difficulty) a suitable one was obtained for an X-ray investigation.

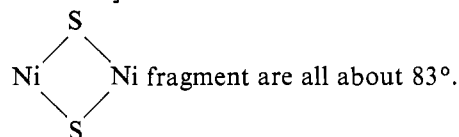
The crystals are monoclinic with twelve $\text{Ni}(\text{SC}_2\text{H}_5)_2$ species in a unit cell of dimensions $a = 12.32$, $b = 16.10$, $c = 11.76 \text{ \AA}$, $\beta = 101^\circ 00'$, and of space group symmetry $\text{P}2_1/\text{n}$. Three-dimensional X-ray data collected photographically with $\text{Mo K}\alpha$ radiation were used to determine the coordinates of the nonhydrogen atoms by a combination of Patterson and successive electron-density syntheses. A subsequent least-squares refinement⁵ yielded final discrepancy factors of $R_1 = 8.0\%$ and $R_2 = 8.4\%$. Details of the structural determination will be published elsewhere.

Solid bis(ethylthio)nickel(II) consists of cyclic hexamers with the molecular configuration shown in Figure 1. The six nickel(II) atoms form a regular planar hexagon by linkage with twelve symmetrically bridging mercaptan groups. Pairs of sulfur atoms are uniformly situated above and below the plane of the nickel ring, but equidistant from each pair of adjacent nickel atoms so as to give each similarly coordinated nickel(II) an approximately square-planar environment of four sulfur

(4) Measured in benzene with a Mechrolab vapor pressure osmometer.

(5) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

atoms. The hexanuclear nickel complex can be considered to arise from the intersection of these planes of sulfur atoms at the nonbonded S-S edges with a dihedral angle of 120° . Within experimental error the nickel and four surrounding sulfur atoms are coplanar; the presumably nonbonded Ni-Ni distances around the hexagon are all equivalent [2.92 \AA , average, with individual e.s.d. of 0.013 \AA] and the Ni-S bond distances likewise [2.20 \AA , average, with individual e.s.d. of 0.017 \AA]. The Ni-S-Ni and S-Ni-S angles in the



A salient feature of the nickel-sulfur framework is that the twelve sulfur atoms thus lie in planar hexagons parallel to the hexagon of nickel atoms, and the open *tetrahedron* so produced has holohedral hexagonal symmetry, $\text{D}_{6h}-6/m2/m2/m$. This hexagonal-shaped triple-layer cylinder of atoms is 2.9 \AA in height (*i.e.*, the perpendicular nonbonded S-S distance between the two planar hexagons of sulfur atoms) and has a nonuniform diameter ranging from 5.85 \AA (average, the nonbonded Ni-Ni distance) to 6.65 \AA (average, the nonbonded S-S distance).

This idealized D_{6h} symmetry of the nickel-sulfur moiety is lowered by the inclusion of the ethyl groups attached to the sulfur atoms. The S-C bonds point alternately either almost radially outwards along an S-S ring diameter or in an upward (or downward) direction nearly perpendicular to the sulfur hexagons. Inclusion of only these methylene carbon atoms gives an idealized symmetry of $\text{D}_{3d}-\bar{3}2/m$. No systematic order exists in the orientations of the methyl carbons, and the symmetry is reduced by their presence to the crystallographically required $\text{C}_i-\bar{1}$.

Special chemical significance is indicated for this type molecule in that the hole formed by the ensemble appears sufficiently large to accommodate axially placed molecules (*e.g.*, acetylenes, CO, UO_2^{2+} , I_2); each nickel(II) possesses a p_z and a d_{z^2} atomic orbital oriented radially and available for combination with centricly

placed atoms or molecules with cylindrical charge distribution. The *tiara* or girdle of nickel-sulfur atoms may be regarded as a cylindrical "mousetrap" waiting to devour any suitably electron-rich or clathrate-prone "mouse." The hexameric association of $[\text{Ni}(\text{SC}_2\text{H}_5)_2]_6$ in solution is consistent with our belief that no significant change in molecular conformation (such as nickel-sulfur bond breaking to give noncyclic chains) occurs on dissolution of the molecular crystal in organic solvents.

Analogous polymeric palladium mercaptides have been prepared^{2,6} and are believed to be similarly hexameric. On the basis of the work described here, it is highly probable that these latter complexes with the congener element palladium will be isostructural with the corresponding nickel complexes. Noteworthy is that the structure of $[\text{Ni}(\text{SC}_2\text{H}_5)_2]_6$ is one of the two models put forward by Hayter and Humiec² for the palladium *n*-propyl mercaptide. Further chemical investigations are in progress.

Acknowledgment. The X-ray work was financially supported both by the Air Force Office of Air Research and Development Command (Contract No. AF-AFOSR-518-64) and by the Sloan Foundation. We also are pleased to acknowledge the partial support of NSF and WARF made by the University Research Committee for the use of the CDC 1604 computer at the University of Wisconsin Computing Center.

(6) F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935).

(7) On leave from the University of Bristol, England.

(8) Alfred P. Sloan Research Fellow.

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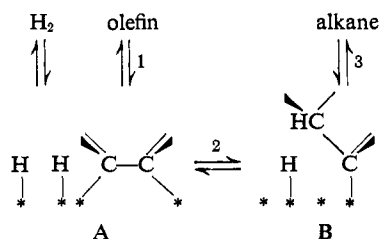
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The Nature of the Diadsorbed Intermediate in Hydrogenation of Olefins

Sir:

The classical Horiuti-Polanyi mechanism for the hydrogenation of olefins on metals of group VIII



is also applied to isotopic exchange between deuterium and alkane¹: the sequence, reaction -3, alternation between di- and monoadsorbed alkane (B and A), reaction 3. If A is diadsorbed alkane, its conformation must be eclipsed.²

It has been argued recently that olefin π -bonded to a single surface atom³ is the preferable form of A. In

(1) J. R. Anderson and C. Kemball, *Proc. Roy. Soc. (London)*, **A226**, 472 (1954).

(2) R. L. Burwell, Jr., B. K. C. Shim, and H. C. Rowlinson, *J. Am. Chem. Soc.*, **79**, 5142 (1957).

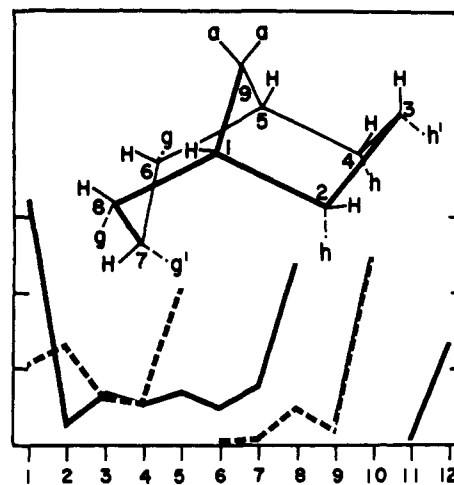


Figure 1. Initial isotopic exchange patterns of bicyclo[3.3.1]nonane at 70° (full line) and cyclopentane at 60° (dashed line).

isotopic exchange of cyclopentane^{1,2} (Figure 1), both forms of intermediate A predict a maximum at d_5 ($\text{C}_5\text{H}_5\text{D}_5$), and both require some additional process to account for initial product more exchanged than d_5 . Indeed, the merely geometrical difference between the two forms is small. Are there molecules which permit a distinction?

In small bicyclic hydrocarbons, neither double bonds (Bredt's rule) nor eclipsed conformations can exist at bridgeheads. As the ring sizes increase, the prohibition against eclipsed conformations relaxes before that against double bonds, for example, bicyclo[3.3.1]nonane, shown in Figure 1 as one of the more favorable conformations of cyclooctane⁴ bridged by methylene. The two hydrogen atoms of the H set at carbon atoms 1 and 2 are eclipsed. Thus, alternation between mono-adsorbed and eclipsed diadsorbed bicyclononane (A and B) permits the exchange of all eight atoms of the H set. If A were π complex one could get from one trimethylene ring to the other only *via* a π -bonded bridgehead olefin. This would be of much too high an energy to function as intermediate A. As shown in Figure 1, the first large maximum in exchange on palladium-on-alumina occurs at d_8 . Thus, at least on palladium, the geometry of eclipsed diadsorbed alkane is acceptable for A; that of a species at all close to olefin is not. Of course, the π complex might be the form in which olefin is first adsorbed.

The argument above specifies geometry but the details of the bonding of A remain unknown. The arguments favoring the π complex depend largely upon the existence of molecular π complexes of olefins, but those are mononuclear, and adsorbed species may well be bonded to several surface atoms as in metallic carbides and nitrides. It has been proposed³ that dialkylacetylenes hydrogenate *via* initial adsorption of acetylene as a linear complex (C') with π bonding to two surface atoms. Here, there are molecular, polynuclear anal-

(3) (a) J. J. Rooney and G. Webb, *J. Catalysis*, **3**, 488 (1964); (b) G. C. Bond and P. B. Wells, *Advan. Catalysis*, **15**, 91 (1964).

(4) Conformation II in K. B. Wiberg, *J. Am. Chem. Soc.*, **87**, 1070 (1965). However, in the solid state, both cyclohexane rings are almost surely in the chair conformation: M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964).