tic acid,[12] thiostreptine shows a singlet (3 protons, 2′-methyl) at $\tau = 8.7$, a doublet (3 protons, ω-methyl) centered at $\tau = 8.4$, $J = 6$ and single protons at $\tau = 6.4$ (3′-H), 4.4 (1′-H) and 1.2 (5-H).

Thiostreptine can be regarded as derived from β,γ-dihydroxyisoleucine and cysteine. It is interesting to note its relationship to the antibiotic hydroxyaspergillic acid,[13] which is a derivative of β-hydroxyisoleucine.

(12) The n.m.r. spectrum was taken soon after preparing the solution. After a few days at room temperature it had changed considerably, and on paper chromatograms a second as yet unidentified spot, yellow with ninhydrin and turning purple, was observed. The same component was detected when solutions, or even solid samples of II, were stored at room temperature.

(13) J. D. Dutcher, *J. Biol. Chem.*, **232**, 785 (1958).

MIKLOS BODANSZKY
THE SQUIBB INSTITUTE JOSEPH ALICINO
FOR MEDICAL RESEARCH CAROLYN A. BIRKHIMER
NEW BRUNSWICK, NEW JERSEY NINA J. WILLIAMS

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NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. LONG-RANGE SPIN COUPLINGS IN VINYLACETYLENE[1]

Sir:

The failure of long-range spin coupling to be observed in the high-resolution proton magnetic resonance spectra of vinylacetylene and propargylaldehyde has been cited[2] as evidence against hyperconjugation as a mechanism for long-range coupling in unsaturated compounds. The reasoning involved has been challenged recently by Hoffman and Gronowitz[3] on theoretical grounds.

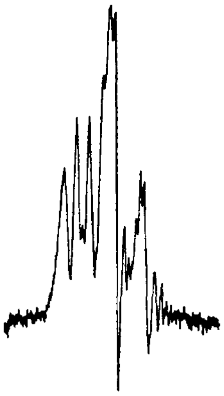

Fig. 1.—Splitting of acetylenic proton resonance of vinylacetylene in benzene solution at room temperature at 60 Mc. taken with Varian A-60 spectrometer. The splitting between the extreme peaks is 2.05 ± 0.05 cps. The appearance of the spectrum is very sensitive to the chemical shifts of the vinyl protons.

It is our belief that further theoretical discussions of this subject must take into account the fact that the couplings in question are by no means negligibly small (*i.e.*, <0.5 cps.) as reported.[2] This is clearly illustrated by Fig. 1 which shows the n.m.r. spectrum of the acetylenic proton of vinylacetylene in benzene solution under very high resolution (<0.20 cps.). The couplings which correspond to the observed splittings are $J_{13} = -2.17$ cps., $J_{14}(cis) = 0.70$ cps., and $J_{14}(trans) = 0.92$ cps. (all ± 0.05 cps.) for vinylacetylene[4] and 0.58 ± 0.05 cps. for propargylaldehyde. The reality of the long-range couplings in vinylacetylene has been further confirmed beyond any question by the proton spectrum of $CH_2{=}CHC{\equiv}CD$, which substance shows the calculated simplification of the vinyl resonances expected for reduction of the magnitude of the relevant couplings by a factor of seven (the H to D gyromagnetic ratio).

A complete analysis of the n.m.r. spectrum of vinylacetylene and its monodeuterated analog will be published later.

(1) Supported in part by the Office of Naval Research and the Undergraduate Research Participation Program of the National Science Foundation.

(2) M. M. Kreevoy, H. B. Charman and D. R. Vinard, *J. Am. Chem. Soc.*, **83**, 1978 (1961).

(3) R. A. Hoffman and S. Gronowitz, *J. Am. Chem. Soc.*, **83**, 3910 (1961).

(4) The signs of the J values are relative to positive signs being taken for couplings within the vinyl group.

(5) National Institutes of Health Postdoctoral Fellow, 1959–61.

CONTRIBUTION NO. 2792 EUGENE I. SNYDER[5]
GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY L. J. ALTMAN
PASADENA, CALIFORNIA JOHN D. ROBERTS

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SQUARE PLANAR-TETRAHEDRAL ISOMERISM AMONG SOME COMPLEXES OF NICKEL(II). A NEW TYPE OF GEOMETRIC ISOMERISM

Sir:

Considerable attention has been given in recent years to the structure of nickel(II) complexes and, as a result, a number of tetrahedral[1] or distorted tetrahedral[2,3] complexes have been characterized, while most of the earlier supposed examples of such complexes have been shown to contain nickel(II) in various octahedral environments. For example, $[NiX_2(P\text{-}n\text{-}Bu\text{-}Ph_2)_2]$ (X = Cl, Br, I) recently were found to be paramagnetic ($\mu_{eff} = 3.2$–3.4 B.M.) and tetrahedral (probably distorted) in the crystalline state. It was thought that the structure of the complexes in solution was either distorted tetrahedral or *cis*-planar and that the magnetic and spectral properties of the solutions could be accounted for in terms of the thermal population of two neighboring energy states, one corresponding to a diamagnetic and the other to a paramagnetic molecule. An alternative interpretation in terms of an equilibrium between a *trans*-planar diamagnetic form and a tetrahedral (or *cis*-planar) paramagnetic form was thought to be less likely.[2]

We have investigated recently the reactions of Ph_2EtP with nickel halides and, from ethanolic solution, have obtained the complexes (I)–(III), (Table I).

An interesting feature of the series (I)–(III) is that the chloride alone is diamagnetic and thus square planar in the solid state. On the other hand, the bromide and iodide are paramagnetic and hence have tetrahedral structures both by analogy with the corresponding complexes of Ph_3P[2] and

(1) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(2) (a) M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton and L. M. Venanzi, *ibid.*, 4816 (1961), and previous work by Venanzi, *et al.*, *ibid.*, 2705 (1961); 719 (1958).

(3) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961), and references therein.

TABLE I

$[NiX_2(PEtPh_2)_2]$	Dec. temp., ° C.	Color	μ_{eff}(B.M.)	Dipole moment (Debye units)	Molecular weight[a] Calcd.	Molecular weight[a] Found
(I) X = Cl	146–151	Dark red	Diamag.	3.2	558	550[b], 535[c]
(II) X = Br[d]	165–175	Dark green	3.20	5.9	647	558[b], 625[c]
(III) X = I	127–138	Brown-red	3.10	7.5	741	745[b], 730[c]
(IV) X = Br	160–175	Dark brown	Diamag.	...	647	575[b]

[a] The molecular weight values (except for (II) and (IV) in benzene) were obtained by boiling-point elevation and were extrapolated to infinite dilution; there was usually a small *decrease* ($< 10\%$) in the observed molecular weight with increasing concentration. (II) and (IV) were measured in 1.3% benzene solution at 37° using a vapor pressure osmometer. [b] Benzene solution. [c] Chloroform solution. [d] First reported in ref. 4.

by the isomorphism of (II) (X-ray powder pattern) with the tetrahedral complexes $[MBr_2(PEtPh_2)_2]$ (M = Co, Zn). In solution, the properties of (I), (II) and (III) are similar to those of the corresponding complexes of Ph_3P and Ph_2-*n*-Bu-P in that they are monomeric, and have high dipole moments and similar spectra in the range 400–1000 mμ. Thus, even $[NiCl_2(PEtPh_2)_2]$ apparently forms a certain amount of polar, paramagnetic species in solution.

These results suggested that the solutions may indeed contain a mixture of geometric isomers and that any equilibrium between them may be greatly affected by the experimental conditions. Qualitative experiments with (II) show that the diamagnetic (red) form is favored by nonpolar solvents and low temperatures and that the paramagnetic (green) form is favored by polar solvents. Thus, (II) gives a dark red solution in carbon disulfide, in which, on cooling to −78°, slowly deposits red crystals (IV), which are dark brown after isolation and are isomeric with (II).

Anal. Calcd. for $C_{28}H_{30}Br_2NiP_2$: C, 52.0; H, 4.7; Br, 24.7; Ni, 9.1; P, 9.6. Found; C, 51.7; H, 4.7; Br, 24.85; Ni, 9.9; P, 9.4. (IV) has an X-ray powder pattern distinct from that of (II), but very similar to that of $[PbBr_2(PEtPh_2)_2]$; this observation and the diamagnetism show that (IV) is square planar in the crystal. The spectrum of (IV) in the solid state is consistent with this and shows a general resemblance to the spectrum of *trans*-$[NiBr_2(P\text{-}n\text{-}Bu_2Ph)_2]$[2]; in particular, (IV) does not absorb in the region 800–1000 mμ, in contrast to (II), which shows a band at 862 mμ, and to other tetrahedral compounds of this type.[2] In benzene solution, the spectra of (II) and (IV) are indistinguishable and both show absorption at 880 mμ ($\epsilon = 130$).

On standing at room temperature, or more rapidly on heating, (IV) gradually turns green, this change being accompanied by an increase in magnetic moment, a constant value of 3.20 B.M. being reached at about 90°. The X-ray powder pattern of the resulting green solid is identical with that of (II). Some salicylaldimine[5] and 1,3-diketone[6] complexes of bivalent nickel show apparently similar temperature-dependent behavior and that usually has been interpreted satisfactorily in terms of square planar–octahedral isomerism, the octahedral structure being achieved by polymerization.[5–7] The evidence presented above, however, shows that green $[NiBr_2(PEtPh_2)_2]$ is tetrahedral (or approximately so) in the solid state and is not polymerized in solution.

(II) and (IV) thus represent the first example of square planar–tetrahedral isomerism among complexes of nickel(II), or indeed of any metal. Further examples have been found among compounds of the type $[NiX_2(PRPh_2)_2]$ and both forms have been isolated in the solid state when X = Br(R = *n*-Pr, *i*-Pr, *n*-Bu) and X = Cl(R = *n*-Bu). We consider that these results afford strong, albeit circumstantial, evidence that, in solution, $[NiX_2(PRPh_2)_2]$ (R = alkyl, Ph) exist as equilibrium mixtures of the square planar and tetrahedral somers.

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MELLON INSTITUTE R. G. HAYTER
4400 FIFTH AVENUE
PITTSBURGH, PA. F. S. HUMIEC

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(5) C. M. Harris, S. L. Lenzer and R. L. Martin, *Aust. J. Chem.*, **14**, 420 (1961).

(6) J. F. Fackler, Jr., and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 3775 (1961).

(7) R. H. Holm, *ibid.*, **83**, 4683 (1961), and references therein.

APPLICATION OF MASS SPECTROMETRY TO STRUCTURE PROBLEMS.[1] VI. NUCLEOSIDES[2]

Sir:

The identification, characterization, and structure determination of nucleosides and related compounds is to a certain extent hampered by their high melting points, their polarity, and insolubility in most organic solvents. Migration in various chromatographic or electrophoretic systems, combined with ultraviolet spectroscopy, is most often used to characterize such molecules. We have, therefore, investigated the applicability of mass spectrometry[3] in this field, although the very low volatility of these compounds would at first seem to preclude this approach. Instead of converting these substances into more volatile derivatives, as in the case of amino acids[4] and peptides,[5] we have utilized free nucleosides, subliming them directly into the ionizing electron beam of the mass spectro-

(1) Part V: K. Biemann and M. Friedmann-Spiteller, *J. Am. Chem. Soc.*, **83**, 4805 (1961).

(2) This investigation was supported by grants from the National Institutes of Health (RG-5472) and the National Aeronautics and Space Administration (NsG 211-62). We wish to thank Dr. Jack J. Fox for samples of synthetic nucleosides and Mr. M. Munroe for invaluable help with the instrumentation.

(3) For a discussion of organic mass spectrometry and the interpretation of spectra see K. Biemann, *Angew. Chemie*, **74**, 102 (1962); *Intern. Ed.*, **1**, 98 (1962); K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

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(5) K. Biemann, F. Gapp and J. Seibl, *ibid.*, **81**, 2274 (1959); K. Biemann, *Chimia* (Switz.), **14**, 393 (1960).