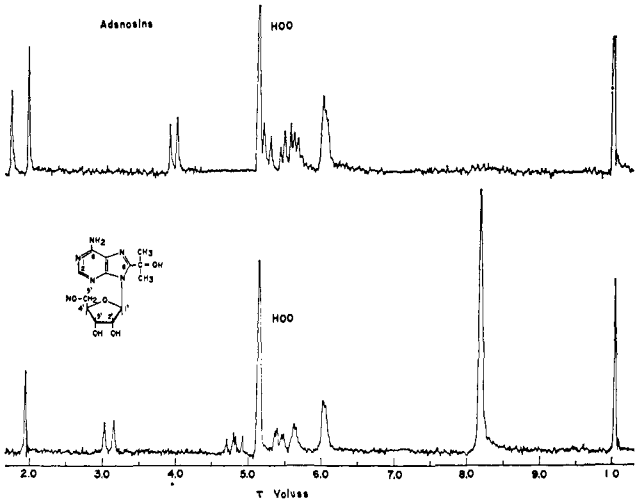

Figure 1. Nmr spectra of adenosine and adenosine–2-propanol adduct in D_2O containing DSS as internal reference. Spectra obtained with a Varian A-60 spectrometer.

its solution in 2-propanol during irradiation with ultraviolet light. These changes are similar to those reported for purine.[1] Furthermore, we found that 2′-deoxyguanosine underwent the same substitution reaction at the 8 position as guanosine. It is noteworthy that reactions resulting in substitution at the C-8 position do not involve a noticeable change in the ultraviolet absorption spectrum of the reaction mixture during irradiation.

The present results indicate that the photochemical reactions of purines and purine nucleosides with 2-propanol lead to characterizable products which are formed in high chemical yields. So far we have noticed that in reactions of 6-amino- or 6-hydroxypurines the 8 position is the most reactive.[8] These reactions seem to be of a free-radical nature[9] since the reaction of adenine and 2-propanol as well as that of caffeine could be initiated in the dark with di-*t*-butyl peroxide at elevated temperature.[10]

The preferred site of attack in the purine ring in a variety of 2- and 6-substituted purines and the detailed mechanism of these reactions are currently being studied, as well as the reactivity of purine moieties in DNA and RNA in photochemical reactions.

(8) *Cf.* A. Albert in "The Chemistry and Biology of Purines," Ciba Foundation Symposium, G. E. W. Wolstenholme and C. M. O'Connor, Ed., J. & A. Churchill, Ltd., London, 1957, p 97, and references cited therein.

(9) *Cf.* M. Ochiai, E. Mizuta, Y. Ashai, and K. Morita, *Tetrahedron*, **24**, 5861 (1968).

(10) H. Steinmaus, I. Rosenthal, and D. Elad, to be published.

(11) Stiftung-Volkswagenwerk Fellow, 1968–1970.

Horst Steinmaus,[11] Ionel Rosenthal, Dov Elad
Department of Chemistry
The Weizmann Institute of Science, Rehovoth, Israel

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An Unusual Example of High-Spin Pentacoordinated Nickel(II)

Sir:

The majority of pentacoordinated high-spin complexes of nickel(II) and other transition elements involve very bulky ligands.[1] These ligands inhibit sterically the attainment of an octahedral arrangement. We wish to report the crystal structure determination of a novel trigonal-bipyramidal nickel complex, bis(acetonethiosemicarbazone)nickel(II) chloride monohydrate. This complex is the first high-spin pentacoordinated species determined by X-ray diffraction where there are only two sulfur atoms, two nitrogen atoms, and a chloride ion in the coordination.

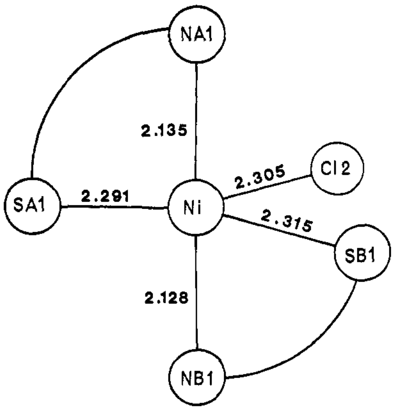

Figure 1. The trigonal-bipyramidal coordination about the nickel atom. The acetonethiosemicarbazone ligand is shown as N–S.

The compound was prepared following the method reported by Ablov and Gerbeleu,[2] who reported only that the compound was paramagnetic. The magnetic susceptibility was found to be 3.4 BM,[3] in agreement with the results of other high-spin pentacoordinated nickel(II) compounds. The yellow-green crystals are orthorhombic with cell dimensions of $a = 21.934 \pm 0.003$, $b = 6.920 \pm 0.001$, and $c = 11.762 \pm 0.002$ Å. The space group is $Pca2_1$ (chosen on the basis of intensity statistics) with four molecules per unit cell. A total of 6185 intensity measurements was made using copper radiation and reduced to a set of 1701 unique reflections, of which 1426 were considered to be observed. The structure was solved by locating the nickel and a sulfur atom in the Patterson function. The remainder of the atoms were located in successive Fourier syntheses. The structure was refined by full-matrix least squares with isotropic thermal parameters to an R, the usual residual, of 11.5% and with anisotropic parameters to an R of 4.7%. The location of the hydrogen atoms and subsequent refinement are in progress.

The crystal is composed of a chloride ion, a water molecule, and the chlorobis(acetonethiosemicarbazone)nickel(II) cation. The coordination about the nickel atom together with the pertinent Ni–X bond distances are illustrated in Figure 1. A comparison of the bond distances with other pentacoordinated species is difficult since no other examples involving sulfur and chlorine have been reported. The most significant nickel(II) complexes whose structures have been determined by X-ray diffraction have been summarized by Sacconi.[4] The equatorial Ni–Cl and Ni–S bonds are about 0.1 Å longer than in a square-planar complex and approxi-

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(1) L. Sacconi, *Pure Appl. Chem.*, **17**, 95 (1968).

(2) A. V. Ablov and N. V. Gerbeleu, *Russ. J. Inorg. Chem.*, **9**, 46 (1964).

(3) G. Beran and G. J. Palenik, unpublished results.

(4) L. Sacconi, "Transition Metal Chemistry," Vol. 4, Marcel Dekker, Inc., New York, N. Y., 1968, p 199.

mately 0.1 Å shorter than in an octahedral complex. While the trend is in the correct direction, any further comparisons are futile because of the lack of data. The axial nitrogen bonds are about 0.2 Å longer than the distances found in square-planar complexes. The lengthening of the axial bonds is typical of trigonal-bipyramidal structures although examples involving nickel are rare.

The three angles SA1-Ni-SB1 (106.4°), SA1-Ni-C12 (120.5°), and SB1-Ni-Cl2 (133.1°) are distorted from the ideal value of 120°. However, the three ligands and the nickel atom are coplanar. The NA1-Ni-NB1 angle of 176.0° is only slightly smaller than the ideal value of 180.0°. These distortions are much smaller than in the case of $Ni(CN)_5^{3-}$ which was reported by Raymond, Corfield, and Ibers.[5]

Since both a water molecule and a chloride ion are available to complete the octahedron, the question of the reason for the pentacoordination is puzzling. A survey of the known octahedral structures[4] indicates that S_4Cl_2 and N_2S_4 coordination about nickel is known. This observation suggests that either the methyl groups are providing steric hindrance or that the coordination is related to electronic effects of the ligand. Further preparative and structural studies of thiosemicarbazones with nickel and other metal salts are in progress to elucidate the factors involved in the formation of the trigonal-bipyramidal structure.

(5) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 7, 1362 (1968).

M. Mathew, Gus J. Palenik
Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada
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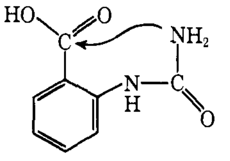
Anionic Nucleophilic Attack upon a Carboxyl Anion

Sir:

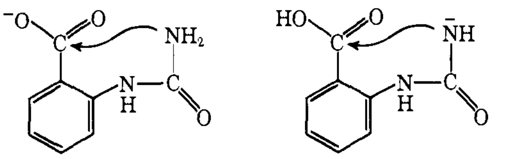
We wish to report the first example of an anionic nucleophilic displacement upon a carboxyl anion (eq 1).

$$\mathrm{Nuc^- + RCOO^- + H_2O \longrightarrow RCONuc + 2HO^-} \qquad (1)$$

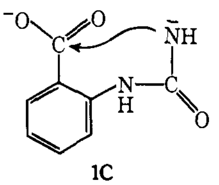
In our hands, N-(*o*-carboxyphenyl)urea (**1**) was found to cyclize in water to yield 2,4-dihydroxyquinazoline (**2**). Without invoking sound chemical reasoning the cyclization process could involve the species **1A**, **1B**, or **1C**. *A priori:* (1) ring closure from **1A** would not appear reasonable since the strong base HO^- is expelled by the weakly basic ureido nitrogen; (2) the involvement of the two species of **1B** cannot be differentiated kinetically; that involving attack of the weakly basic ureido nitrogen would appear impossible but displacement of HO^- by the strongly basic ureido nitrogen anion would be the most reasonable of all the alternate mechanisms; and (3) attack of an anionic center upon a carboxyl anion as in **1C** has no precedence in organic chemistry and would appear impossible. Mechanisms involving species **1A**, **1B**, and **1C** may be kinetically differentiated. At pH values much greater than the pK_a of the carboxyl group, the rate of reaction of **1A** should *decrease* linearly with decrease in a_H, the rate of reactions involving **1B** should be insensitive to a_H, while the rate of reaction of **1C** should *increase* linearly with decreasing a_H. The pseudo-first-order rate constants for the formation of **2** from **1** were found to *increase* linearly with decreasing $a_{H'}$.[1] In Table I are provided the pH values employed, the experimental values of k_{obsd}, and the second-order rate constants calculated from the expression $k_2[\mathbf{1}]\cdot[HO^-]$. Examination of Table I reveals that k_2 remains constant, within experimental error, over greater than a 100-fold change in a_H.



1A



1B

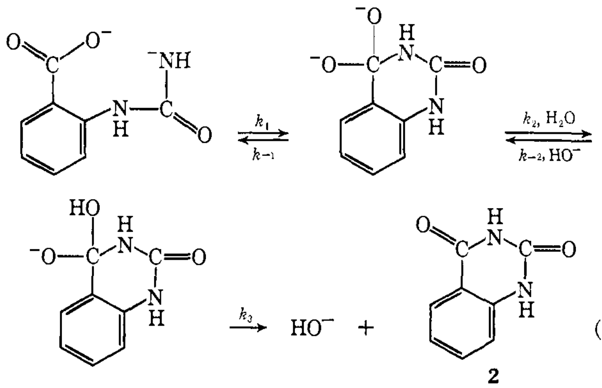


1C

Table I. Pseudo-First-Order Rate Constants (k_{obsd}) and Calculated Second-Order Rate Constants (k_2) as a Function of pH

pH	10^6k_{obsd}, sec^{-1}	10^4k_2, l. mol^{-1} sec^{-1}
13.70	410	5.56
13.01	85	5.66
12.61	34	5.66
11.34	1.7	5.42

To obviate expulsion of O^{2-} from **1C** one of several plausible mechanisms would be that of eq 2, with k_1 rate determining.



2 (2)

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[1] Rate determinations were carried out at 30°, μ = 1.0 with KCl in the absence of buffer by employing a special spectrophotometric titration cell attached to a Cary 15 recording spectrophotometer and a Radiometer pH-stat assembly. The product **2** was identified at the end of selected kinetic runs by spectrophotometric titration in the reaction cell (pK_a = 9.60). The pK_a of an authentic sample of **2** (N. A. Lange and F. E. Sheibley, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 79) was determined to be 9.60 (NH function between the two C=O groups). Ultraviolet spectra of product and authentic **2** are identical at varying pH values.