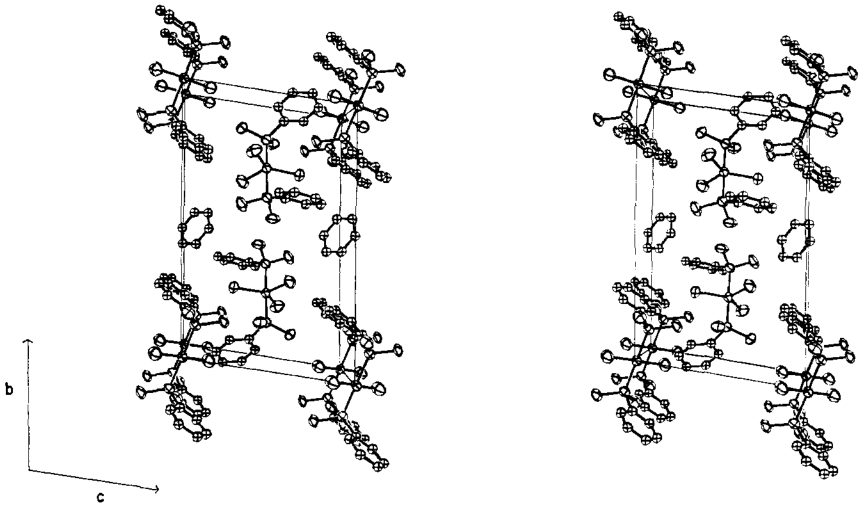

Figure 1. A stereoscopic view of the unit cell of $NiBr_3(P(CH_3)_2(C_6H_5))_2 \cdot 0.5NiBr_2(P(CH_3)_2(C_6H_5))_2 \cdot C_6H_6$. Here and in Figure 2 hydrogen atoms have been omitted for the sake of clarity.

The collection of the X-ray data and the solution and refinement of the structure were carried out by standard methods. The conventional *R* factor for the 2514 intensities above background is 5.4%. The highest peak on a final difference Fourier map is 1.1 e/Å$^3$, approximately 30% of the height of a carbon atom in this compound.

The structure consists of well-separated four- and five-coordinate molecules, with no indications of intermolecular association *via* bromide bridges (Figure 1). The *trans* square-planar molecule, $NiBr_2(P(CH_3)_2(C_6H_5))_2$, is crystallographically required to possess a center of symmetry. The Ni–P and Ni–Br bond lengths of 2.251 (3) and 2.297 (2) Å, respectively, appear to be normal for Ni(II) square-planar complexes. The P–Ni–Br angle is 90.45 (8)°.

The five-coordinate $NiBr_3(P(CH_3)_2(C_6H_5))_2$ molecule has a trigonal-bipyramidal geometry, with the two phosphines occupying the axial positions and the three bromines in the equatorial plane. The Ni and three Br atoms are coplanar, and the P–Ni–P linkage is nearly linear (178.8 (1)°). This geometry is illustrated in Figure 2; selected bond distances are also presented. There is a significant distortion from idealized trigonal-bipyramidal geometry; the $Ni_2$–$Br_3$ bond length of 2.375 (2) Å is longer than the other two distances of 2.339 (2) and 2.349 (2) Å, and the angle opposite this long bond is expanded to 132.71 (9)° from the expected 120°. The complex contains Ni(III) in a low-spin $d^7$ electronic configuration and is subject to Jahn–Teller considerations which should remove the degeneracy of the $d_{xy}$ and $d_{x^2-y^2}$ orbitals in $D_{3h}$ symmetry, resulting in the observed geometry.

We have examined esr spectra of both I and II as solids at room temperature and in a frozen toluene solution at 77°K. The absence of a resonance is evidence against an assignment of these complexes as "metal-stabilized radical-ligand" systems[9,10] since an anisotropic pattern with $\langle g \rangle$ values near 2.0–2.1 would be expected.[4,9,10] For a Ni(III) formulation, the predicted anisotropic *g* values may not be observed because of the short spin-lattice relaxation time of the pentacoordinate system.[12] The measured magnetic moment of II was 1.71 BM per nickel. By considering that one-third of the molecules are diamagnetic, the recalculated magnetic moment is 2.09 BM per Ni(III) ion, in good agreement with the value obtained originally on I.

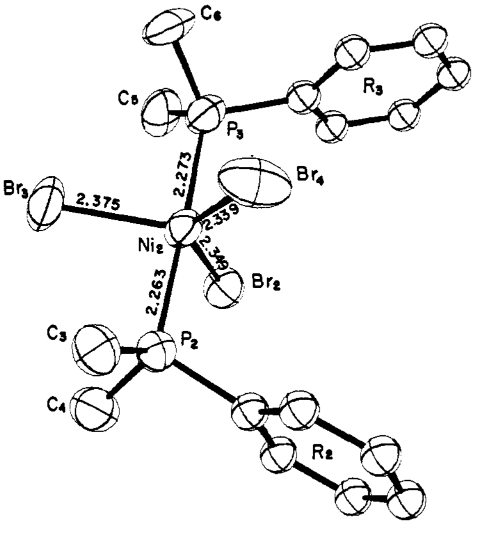

Figure 2. A perspective drawing of $NiBr_3(P(CH_3)_2(C_6H_5))_2$.

**Acknowledgments.** We thank the National Science Foundation for its financial support of this research.

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[12] G. F. Kokoszka and G. Gordon in "Techniques of Inorganic Chemistry," Vol. VII, H. Jonassen and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1968, p 151.

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## Photochemical and $\gamma$-Ray-Induced Reactions of Purines and Purine Nucleosides with 2-Propanol

*Sir:*

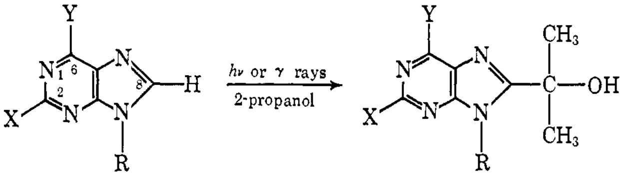
The photochemical reactions of purine and alcohols as well as the radiation- and ultraviolet-induced reac-

Table I. Ultraviolet- and Radiation-Induced Reactions of Purines and Purine Nucleosides with 2-Propanol

| Purine or purine nucleoside | Product (II) Yield,[a] % | Product (II) Mp, °C | Source of radiation | Sensitizer | $\phi$ | $g$ value |
|---|---|---|---|---|---|---|
| Adenine (Ia) | 69 | 249–251 | Uv;[b] $\lambda$ >290 nm[c] | Acetone | | |
| | 59 | | Uv; $\lambda$ >260 nm[d] | | 0.0012 | |
| | 81 | | $\gamma$ rays[e] | Acetone | | 2.1 |
| Adenosine (Ib) | 53 | 227–230 | Uv; $\lambda$ >290 nm | Acetone | | |
| | 62 | dec | Uv; $\lambda$ >260 nm | | 0.0018 | |
| | 54 | | $\gamma$ rays | Acetone | | 1.1 |
| Guanosine (Ic) | 45 | 211–213 | Uv; $\lambda$ >290 nm | Acetone | | |
| | 68 | | $\gamma$ rays | Acetone | | 0.5 |
| Hypoxanthine (Id) | 27 | | Uv; $\lambda$ >290 nm | Acetone | | |

[a] Based on purine employed. [b] Hanovia 450-W high-pressure mercury vapor lamp. [c] Pyrex filter. [d] Corex filter. [e] $^{60}$Co $\gamma$ source Gamma cell 220 (Atomic Energy of Canada Ltd., Ottawa, Canada). Dose rate = $1.27 \times 10^{18}$ eV ml$^{-1}$ min$^{-1}$.

tions of alcohols and caffeine have been reported recently.[1,2] It has been shown that addition of the alcohol occurs across the 1,6 double bond of purine,[1] whereas with caffeine substitution at the C-8 position takes place.[2] We wish to report now the photochemical and $\gamma$-ray-induced reactions of nucleic acid occurring purines and purine nucleosides with 2-propanol, all of which lead to substitution at the C-8 position of the purine ring system, the substituent being the $C(CH_3)_2OH$ group. The reactions could be induced directly by short-wavelength ultraviolet light or sensitized with acetone when light of longer wavelength (>290 nm) was employed, as well as by $\gamma$ rays. The reactions studied and the products isolated are described in Table I.



IIa-d

Ia, X = H; Y = $NH_2$; R = H (adenine)
b, X = H; Y = $NH_2$; R = ribose (adenosine)
c, X = $NH_2$; Y = OH; R = ribose (guanosine)
d, X = H; Y = OH; R = H (hypoxanthine)

In a typical experiment a solution of adenosine (750 mg), water (50 ml), 2-propanol (80 ml), and acetone (80 ml) was irradiated with ultraviolet light at room temperature under nitrogen for 11 hr. Solvents were removed under reduced pressure and the residue was chromatographed (ascending) on 9-in. strips of Whatman No. 17 paper in a mixture of 1-butanol–water–concentrated ammonia (86:9:5, v/v). The product zone was detected with a Mineralight lamp, cut, and eluted with methanol, leading to IIb (502 mg).

The structures of the products were determined by elemental analyses, as well as by nmr and mass spectra. The products showed the appropriate molecular peaks or fragmentation pattern in the mass spectra which were in agreement with the proposed 1:1 "adduct" structures. The ultraviolet absorption spectra of the products were the same as those of the starting materials, indicating that the absorbing chromophore has not changed during the reaction.

**Nmr Data.** Guanosine has only one C–H proton in the purine ring system, *i.e.*, the one at the 8 position, which appears in the nmr spectrum at $\tau$ 1.97 (DMSO-$d_6$).[3] The guanosine–2-propanol photoadduct does not show this band in the spectrum, thus indicating that the hydrogen at C-8 was substituted. It shows, in addition, the signal at $\tau$ 8.26 ($D_2O$) of the two methyls of the $C(CH_3)_2OH$ group. Adenosine has two C–H protons in the purine ring system, *i.e.*, the ones at the C-8 and the C-2 positions, absorbing at $\tau$ 1.72 and 1.97 ($D_2O$), respectively.[4] The nmr spectrum of the adenosine–2-propanol adduct does not show the band at $\tau$ 1.72, indicating that substitution took place at the C-8 position. Further evidence for substitution occurring at C-8 is given by deuterium exchange experiments. We found that deuterium exchange in adenosine with $D_2O$ at 105° led to the disappearance of the band at lower field, indicating that the C-8 proton had been exchanged, while the C-2 proton remained intact. A similar effect has been reported for purine[5] and substituted purines,[6] where only the C-8 proton exchanged for deuterium with $D_2O$ at 105°. The adenosine–2-propanol photoadduct was found by treatment under these conditions to have no exchangeable protons in the purine ring. This supplies further evidence for the absence of the C-8 proton in the photoadduct. Similar results were obtained with the other purines and purine nucleosides. A typical nmr spectrum of a photoadduct is that of IIb which is given in Figure 1.[7]

The photoreactions of the substituted purines and 2-propanol reported, as well as those of the nucleosides, involve substitution at the C-8 position of the purine moiety, as compared to addition of the alcohol across the 1,6 double bond in purine itself. It seems that the sugar moiety does not affect the site of attack in the purine ring since an addition reaction, most probably across the 1,6 bond, takes place in purine riboside, as judged from the changes in the ultraviolet spectrum of

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(1) H. Linschitz and J. S. Connolly, *J. Am. Chem. Soc.*, **90**, 2979 (1968); J. S. Connolly and H. Linschitz, *Photochem. Photobiol.*, **7**, 791 (1968).

(2) D. Elad, I. Rosenthal, and H. Steinmaus, *Chem. Commun.*, 305 (1969).

(3) The nmr spectra were recorded in $D_2O$ or DMSO-$d_6$ containing 1% (w/w) DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as a reference standard (Merck Sharp & Dohme of Canada, Ltd., Montreal). The chemical shifts of the protons in the purines have been reported to be concentration dependent (see, for example, ref 4); however, the relative positions of the peaks do not change with concentration, *e.g.*, the C-2 proton in adenosine always appears at a higher field than the C-8 proton.

(4) *Cf.* A. D. Broom, M. P. Schweizer, and P. O. P. Ts'o, *J. Am. Chem. Soc.*, **89**, 3612 (1967); P. O. P. Ts'o, N. S. Kondo, M. P. Schweizer, and D. P. Hollis, *Biochemistry*, **8**, 997 (1969), and references cited therein.

(5) M. P. Schweizer, S. I. Chan, G. K. Helmkamp, and P. O. P. Ts'o, *J. Am. Chem. Soc.*, **86**, 696 (1964).

(6) J. M. Rice and G. O. Dudek, *ibid.*, **89**, 2719 (1967).

(7) The differences in the chemical shifts and coupling constants of the sugar protons in adenosine and the photoproduct in the $\tau$ 3–7 region probably result from conformational changes in the ribose moiety.

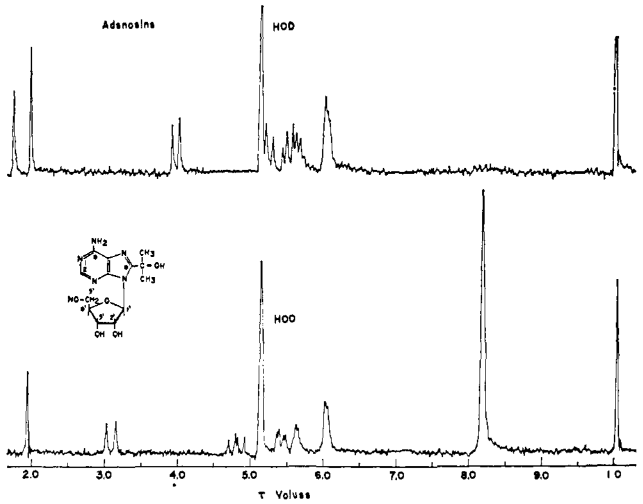

Figure 1. Nmr spectra of adenosine and adenosine–2-propanol adduct in $D_2O$ containing DSS as internal reference. Spectra obtained with a Varian A-60 spectrometer.

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.

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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.

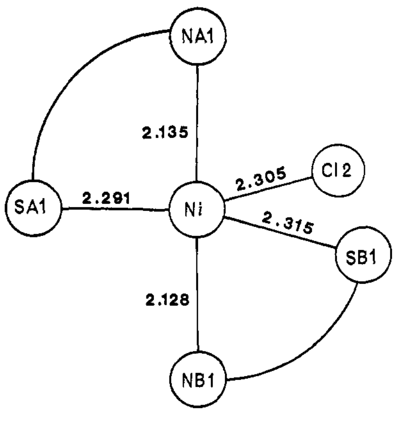

Figure 1. The trigonal-bipyramidal coordination about the nickel atom. The acetonethiosemicarbazone ligand is shown as N–S.

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-

(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.