passed through a U trap cooled to −50°. The crude product collected in the trap (130 mg, 79%) was recrystallized from ethanol to give 51 mg (31%) of II.

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Correspondence

The So-Called *cis–trans* Isomerism of Bis(isothiocyanato)tetra(pyridine)iron(II)[1]

Sir:

There is currently considerable interest in the preparation and properties of mixed-ligand complexes formed between transition metal ions, pyridine, and various anions.[2-5] This communication is concerned with the compound $Fe(py)_4(NCS)_2$. It was reported more than 50 years ago that this compound exists in two forms: a yellow form, prepared by Grossmann and Hunseler,[6] and a violet form, prepared by Spacu.[7,8] Both forms give violet solutions in chloroform, benzene, or toluene and yellow solutions in polar solvents such as pyridine, methanol, or ethanol.[7-9] The composition and structure of the violet form have been the subject of controversy for many years.[9-12] Recently, however, Spacu, *et al.*,[9] concluded from a series of physical measurements (dipole moments[13] and infrared and visible spectra) and chemical measurements (the reactions of the two forms with 2,2′-bipyridine and 1,10-phenanthroline) that the colors were due to *cis–trans* isomerism and that the yellow form was the *cis* isomer.

Our interest in these compounds arose from a desire to study *cis–trans* isomerism in high-spin iron(II) compounds *via* the Mössbauer technique in order to determine what influence this type of isomerism may have on the Mössbauer spectra. The only previous examples of true *cis–trans* isomers studied *via* the Mössbauer effect were several pairs of low-spin iron(II) compounds.[14] In these compounds the change in configuration results in a rather large and predictable change in the quadrupole splittings and in the chemical shifts of the Mössbauer patterns.

The yellow form was prepared by gradually adding 250 ml of a solution containing 9 g of hydrated ferrous perchlorate and a pinch of ascorbic acid to 400 ml of a solution containing 4 g of ammonium thiocyanate and 10 ml of pyridine. The yellow precipitate was filtered off and washed with a mixture consisting of 85% ethanol, 5% water, and 10% pyridine. The complex was recrystallized from a mixture consisting of 65% ethanol, 25% water, and 10% pyridine and dried *in vacuo* for 30 min. *Anal.* Calcd for $Fe(py)_4(NCS)_2$: Fe, 11.4; SCN^-, 23.8. Found: Fe, 11.4; SCN^-, 24.1.

The violet form was prepared by recrystallizing the yellow form from chloroform. According to Spacu, *et al.*,[9] this procedure is supposed to convert the *cis* isomer to the *trans* isomer. It was found instead that solutions prepared by dissolving the yellow form in air-free chloroform (or in air-free benzene) did not turn violet. The solutions did, however, turn violet gradually upon exposure to air, and very rapidly upon the addition of a few drops of a dilute solution of bromine in chloroform. Moreover, the violet color disappears upon the addition of ascorbic acid or upon bubbling hydrogen through the solution in the presence of a palladium catalyst and returns upon exposure to air. This suggests that the color change from yellow to violet results from the oxidation of the iron(II) complex and is not due to isomerization, a conclusion is substantial agreement with that previously reached by Rosenheim.[12] The iron(III) in the two forms was determined by dissolving the crystals in air-free 1 *M* $HClO_4$ and estimating the iron(III) in the resulting solutions polarographically. The yellow form contained 0.02% of iron(III) while the violet form contained 0.40% of iron(III). Violet crystals containing up to 1.6% of iron(III) have been obtained by dissolving the yellow form in oxygen-saturated chloroform containing a few drops of pyridine and allowing the excess solvent to evaporate over several hours. The color change produced by the addition of excess alcohol or pyridine to chloroform solutions of the violet form can be explained by the dissociation of the iron(III) complex in alcohol and by a combination of dissociation and reduction of the iron(III) complex in pyridine.

The conclusion that the yellow and violet forms are not geometrical or linkage isomers was confirmed by Mössbauer and X-ray studies. The Mössbauer spectra of the two forms are identical within the experimental

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *Inorg. Chem.*, **5**, 635 (1966).

(3) R. V. Biagetti and H. M. Haendler, *ibid.*, **5**, 383 (1966).

(4) C. W. Frank and L. B. Rogers, *ibid.*, **5**, 615 (1966).

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(6) H. Grossman and F. Hunseler, *Z. Anorg. Chem.*, **46**, 370 (1905).

(7) G. Spacu, *Ann. Sci. Univ. Jassy*, **8**, 175 (1914); **9**, 347 (1915).

(8) G. Spacu, *Z. Anorg. Allgem. Chem.*, **216**, 165 (1933).

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(10) A. Rosenheim, E. Roehrich, and L. Trewendt, *Z. Anorg. Allgem. Chem.*, **207**, 97 (1932).

(11) R. Asmussen, *ibid.*, **218**, 425 (1934).

(12) A. Rosenheim, *ibid.*, **216**, 173 (1933).

(13) Only the dipole moment of the violet form was measured.

(14) N. E. Erickson, Ph.D. thesis, University of Washington, Seattle, Wash., 1964; R. R. Berrett and B. W. Fitzsimmons, *Chem. Commun.*, 91 (1966).

error of the measurements.[15] The quadrupole splitting ($\Delta E = 1.53 \pm 0.04$ mm sec^{-1}, independent of temperature from room temperature down to liquid nitrogen temperature) corresponds to an orbital doublet ground state,[16] while the chemical shift (δ +1.16 ± 0.04 mm sec^{-1} at room temperature, relative to an iron foil absorber) is characteristic of high-spin iron(II) complexes. The orbital doublet ground state implies that both forms possess a fairly high degree of geometrical and orbital symmetry. Such a ground state can be realized by any one of several arrangements of pyridine rings in the *trans* isomer but by only one, rather unlikely, arrangement of pyridine rings in a *cis* isomer.

The X-ray patterns of single crystals of the two forms were also found to be identical with regard to both spot positions and relative intensities.[15,17] The cell dimensions of the two forms are $a = 12.38 \pm 0.02$ A, $b = 13.04 \pm 0.02$ A, $c = 16.42 \pm 0.02$ A, and $\beta = 118.1 \pm 0.1$. Moreover, the crystals are isomorphous with $Ni(py)_4(NCS)_2$ and $Co(py)_4(NCS)_2$, whose structures have been determined by Porai–Koshits and Antsishkina.[18] In these compounds the thiocyanate groups are *trans* to each other and the nitrogen end of the thiocyanate is attached to the metal. The similarity of the X-ray spectra of the yellow and violet forms together with the fact that the crystals are isomorphous with $Ni(py)_4(NCS)_2$ and $Co(py)_4(NCS)_2$ establishes that both forms have a *trans* structure and rules out the possibility of linkage isomerism.

We conclude, therefore, that the yellow form (λ_{max} ~365 mμ in chloroform) has a *trans*-octahedral configuration[19] and is not the *cis* isomer as claimed by Spacu, *et al.*,[9] and that the violet form (λ_{max} ~525 mμ in chloroform[20]) is essentially an impure version of the yellow form, the impurity being traces of iron(III).

[15] The Mössbauer and X-ray measurements were not sufficiently sensitive to detect the small amount of iron(III) (0.40%) present in the violet form.

[16] G. R. Hoy and F. de S. Barros, *Phys. Rev.*, **139A**, 929 (1965).

[17] These measurements were performed by Dr. Elmer O. Schlemper at the Chemistry Department, Brookhaven National Laboratory, Upton, N. Y.

[18] M. A. Porai-Koshits and A. S. Antsishkina, *Soviet Phys.-Cryst.*, **3**, 694 (1958).

[19] Goodgame, *et al.*,[2] have also proposed that (yellow) $Fe(py)_4(NCS)_2$ has a *trans*-octahedral structure on the basis of the similarity of the X-ray powder photographs of $Fe(py)_4(NCS)_2$ and $Ni(py)_4(NCS)_2$.

[20] The peak at 525 mμ in the spectrum of the violet form is present in addition to the peak at 365 mμ, which is also found in the spectrum of the yellow form.

CHEMISTRY DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

NILS E. ERICKSON
NORMAN SUTIN

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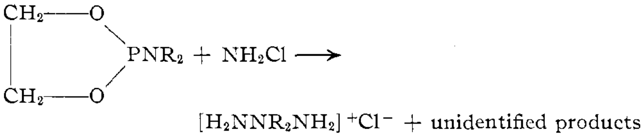
Triazanium ($NH_2NR_2NH_2^+$) Salts by Chloramination Reactions

Sir:

No unsubstituted hydronitrogen in the series N_nH_{2n+2} of higher molecular weight than N_2H_4 is known except for the possible formation of N_4H_6 (tetrazane) as a solid at −195°. According to Rice and Scherber[1] this material decomposes rapidly at −178° to nitrogen and ammonia. A very few substituted triazanes have been reported and none of these is a simple alkyl or aryl derivative, and in many instances the claimed triazane derivatives are of doubtful composition and not well-established identity. Recently, Gösl claimed the formation of a dialkyltriazanium salt[2] by the reaction of 1,1-dimethylhydrazine with hydroxylamino-O-sulfonic acid but gave no analytical data. Gösl indicated that studies of the infrared spectrum indicated that the dimethyltriazanium ion has the structure $[H_2NN(CH_3)_2NH_2]^+$, but no details were given to confirm this.

We wish to report the preparation of a series of new trizanium chlorides through the use of the chloramination reaction. Two procedures have been employed, apparently for the first time: (1) the treatment of a benzene solution of a 2-dialkylamino-1,3,2-dioxophospholane with a gaseous mixture of chloramine and excess ammonia, produced by the gas-phase chlorination of ammonia[3]



and (2) the treatment of a benzene solution of a 1,1-dialkylhydrazine with a gaseous mixture of ammonia and chloramine

$$R_2NNH_2 + NH_2Cl \longrightarrow [H_2NNR_2NH_2]^+Cl^-$$

Compounds prepared by the first procedure include the following.

2,2-Dimethyltriazanium Chloride.—The yield of purified product was 51%; mp 133.5–134.0° dec. *Anal.* Calcd for $C_2N_3H_{10}Cl$: C, 21.53; H, 9.03; N, 37.66; Cl, 31.77. Found: C, 21.20; H, 9.00; N, 37.78; Cl, 31.85.

2,2-Diethyltriazanium Chloride.—The yield of purified product was 62%; mp 135–136° dec. *Anal.* Calcd for $C_4N_3H_{14}Cl$: C, 34.41; H, 10.10; N, 30.09; Cl, 25.39. Found: C, 34.17; H, 10.21; N, 29.87; Cl, 25.39.

2,2-Cyclotetramethylenetriazanium Chloride.—The yield of purified product was 41%; mp 121–123° dec. *Anal.* Calcd for $C_4N_3H_{12}Cl$: C, 34.91; H, 8.79; N, 30.54; Cl, 26.04. Found: C, 33.08; H, 8.64; N, 29.55; Cl, 26.04. Though the carbon analysis is low, the remainder of the analytical data combined with the infrared and nmr data leave no doubt concerning the identity of this compound.

2,2-Dimethyltriazanium chloride was also prepared by the second procedure. The yield of purified product was 40%; mp 133–134° dec. *Anal.* Calcd for $C_2N_3H_{10}Cl$: C, 21.53: H, 9.03; N, 37.66; Cl, 31.77. Found: C, 21.34; H, 9.08; N, 37.54; Cl, 31.90.

[1] F. O. Rice and F. Scherber, *J. Am. Chem. Soc.*, **77**, 291 (1955).

[2] R. Gösl, *Angew. Chem. Intern. Ed. Engl.*, **1**, 405 (1962).

[3] H. H. Sisler, F. Neth, R. Drago, and D. Yaney, *J. Am. Chem. Soc.*, **76**, 3906 (1954).