with xenon and with krypton at low temperatures. No reaction was observed with krypton up to −78°, where O_2F_2 rapidly decomposes. Xenon, on the other hand, was converted quantitatively to a yellow solid by reaction with a large excess of O_2F_2 at −118°. When this solid was sublimed at 50°, high yields of xenon difluoride were obtained. The nature of the gases evolved during the process of warming the initial solid from −78° to room temperature indicated the presence of unstable oxygen-containing compounds of xenon which we were unable to identify.

Experimental

Reaction of Dioxygen Difluoride with Xenon.—The method of preparing dioxygen difluoride used in this work has been described by Streng.[1] The reagent was generated at −196° in a U-shaped Kel-F discharge tube and distilled at −78° through a 3-in. length of metal tubing (cooled with Dry Ice) to a Kel-F reaction tube maintained at −196°. A measured quantity of xenon had previously been condensed into the bottom of the reaction tube. The xenon–dioxygen difluoride mixture was then warmed to −118° (ethyl bromide slush bath) and held at that temperature for 2 hr. The temperature was measured with a low-temperature thermometer. The vapor pressure of dioxygen difluoride at −118° is approximately 16 mm. and that of xenon about 400 mm. In every experiment the xenon was virtually quantitatively converted to a yellow solid having a negligible vapor pressure up to −21°. The excess dioxygen difluoride decomposed to oxygen and fluorine when the reactor and its contents were stored overnight at −78°.

Purification of Xenon Difluoride.—After the excess dioxygen difluoride had decomposed at −78° and the decomposition gases were removed from the tube, the solid residue became white. Analysis of the gases recovered from the reactor never revealed more than trace quantities of xenon. The white solid was outgassed under vacuum at −21° for 2–3 hr. Volatile impurities removed by this treatment were CO_2, COF_2, CF_4, C_2F_6, SiF_4, and SF_6. (The latter four compounds are impurities in the fluorine, while COF_2 is commonly formed in small amounts in the preparation of the dioxygen difluoride.) The lower part of the evacuated Kel-F tube containing the white solid product was then immersed in a bath at 50°. The upper part of the tube was cooled by wrapping it with a band of Pyrex wool which was kept saturated with acetone. Transparent crystals condensed on the cooler upper walls of the tube. Gases evolved during this process were composed of variable amounts of xenon, oxygen, and fluorine. A typical analysis of the off-gases obtained in this way was $Xe:O_2:F_2 = 2.8:1:1$. The crystals were removed from the tube in a drybox. They were identified as pure xenon difluoride by powder diffraction and single crystal X-ray analysis ($a = 4.315$, $c = 6.990$, space group 14/mmm).[2] A material balance for one experiment showed the yield of xenon difluoride was 98% of theory. In this run 4.25 mmoles of xenon was used. The amount of purified xenon difluoride obtained was 0.7052 g. (4.16 mmoles).

Evidence for Formation of an Oxygen-Containing Compound of Xenon.—When the product, which had been out-gassed at −21°, was recooled to −78°, oxygen, xenon, and xenon difluoride appeared in its mass spectrometric fragmentation pattern. As the sample was warmed to −21°, these same constituents, as well as traces of xenon tetrafluoride, appeared in the mass spectrometric pattern. When the sample was held at room temperature, the pattern consisted primarily of xenon difluoride with lesser amounts of xenon tetrafluoride and oxygen.

During sublimation of the product under vacuum, significant amounts of xenon, oxygen, and fluorine were evolved. In one case when the solid product was heated to 49° under vacuum to recrystallize it, a mixture of Xe, O_2, and F_2 was evolved in a ratio of 2.7:1:1. In several experiments small amounts of a clear liquid were distilled from the solid products at room temperature *in vacuo*. These liquid distillates decomposed on standing for several hours at room temperature, yielding mixtures of xenon, oxygen, and fluorine. Determinations of the relative quantities of the components of the decomposition gases gave widely varying results from run to run.

It is interesting to note that Streng, *et al.*,[3] have reported that significant yields of xenon oxyfluorides are obtained by the reaction of xenon with oxygen difluoride in an electric discharge and by thermal reactions of xenon with oxygen difluoride or oxygen-fluorine mixtures. The stabilities of the oxygenated products obtained from oxygen difluoride are apparently much greater than observed for the products obtained in this study.

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A Spectrophotometric Study of the Geometrical Isomers of Tris(2-picolylamine)nickel(II) Chloride

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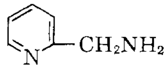
Recently, spectrophotometric studies of some metallic chelates of 2-picolylamine (2-aminomethylpyridine) including the tris chelate of hexacoordinated nickel(II) were reported.[2] However, since 2-picolylamine (pic) is an unsymmetrical ligand



being structurally intermediate between ethylenediamine and 2,2′-dipyridyl, the ion $Ni(pic)_3^{2+}$ could exist in two geometrical isomers. We have isolated and identified these isomers and investigated their absorption spectra. Considering the method of preparation previously reported for this compound, it is probable that the published spectra[2,3] are for isomeric mixtures.

Experimental

Preparation of Tris(2-picolylamine)nickel(II) Chloride Dihydrate.—The complex was prepared by the method of Sutton.[3] The 2-picolylamine was obtained from Aldrich Chemical Co. and used without further purification. Heating the dihydrate at 110° resulted in a rupture of the crystal lattice, leaving a violet microcrystalline powder.

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(1) National Science Foundation Undergraduate Summer Research Participant.

(2) S. Utsuno and K. Sone, *Bull. Chem. Soc. Japan*, **37**, 1038 (1964).

(3) G. J. Sutton, *Australian J. Chem.*, **13**, 74 (1960).

Separation of the Geometrical Isomers.—Any excess ligand was removed by washing the purple powder in a 90% ether–ethanol mixture. Treatment with anhydrous 2-propanol resulted in a brown solution and a purple solid. Evaporation of the brown solution yielded yellow-brown crystals which were washed with ether and air-dried. The purple solid, not effected by additional 2-propanol, was likewise washed and air-dried. If an aqueous solution of the original violet powder was heated and evaporated to dryness before the treatment with 2-propanol, the yield of the brown substance was increased.

Instrumental.—Infrared spectra were obtained with a Beckman IR-5A sodium chloride spectrophotometer using KBr disks. The ultraviolet, visible, and near-infrared spectra were measured with a Cary Model 14 spectrophotometer employing 10-mm. silica cells.

Results and Discussion

Infrared spectra of both the brown and purple products resulted in essentially identical curves. Both forms were slightly hygroscopic, and the elemental analyses, assuming the dihydrate, were practically identical.

Anal. Calcd. for $C_{18}H_{28}N_6Cl_2O_2Ni$: C, 44.2; H, 5.7; N, 17.1; Cl, 14.4. Found (brown product): C, 44.5; H, 5.8; N, 17.0; Cl, 14.1. Found (purple product): C, 44.6; H, 5.8; N, 16.9; Cl, 13.9.

That these two products are isomers of the same compound is evident because heated 2-propanol solutions of the brown species produced purple crystals on standing a few days, while heated aqueous solutions of the purple form evaporated to dryness yielded additional brown product upon treatment with anhydrous 2-propanol. Since they react upon refluxing to yield different ratios of the isomers, it can be concluded that the stereochemistry is at least to some extent kinetically controlled. The decomposition temperatures of the brown and purple isomers are 200 and 268°, respectively. Aqueous solutions of both isomers of $Ni(pic)_3^{2+}$ are stable at room temperature, whereas at 50° preliminary results indicate that equilibrium is reached within 24 hr.

The curves obtained from the ultraviolet, visible, and near-infrared spectra of aqueous solutions of the hydrated isomers by plotting the logarithm of the molecular extinction coefficient against the wave length in mμ are given in Figure 1. The absorption maxima and the corresponding molecular extinction coefficients, ϵ, are summarized in Table I. Concentrations from 6×10^{-2} to 1×10^{-2} *M* were used in obtaining spectra in the visible and near-infrared regions. In the ultraviolet range concentrations from 1×10^{-4} to 1×10^{-5} *M* were employed and in all cases Beer's law was obeyed for both compounds.

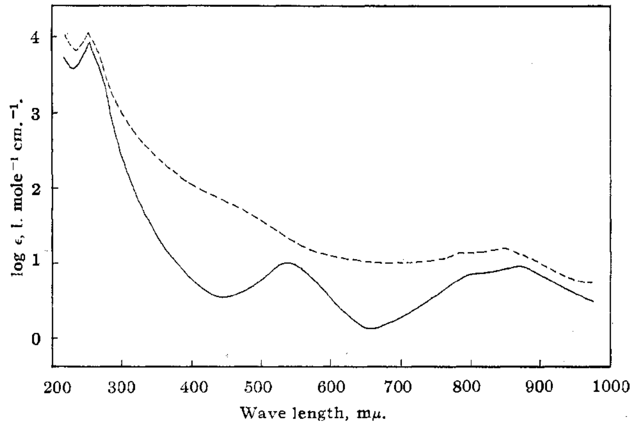

Figure 1.—Absorption spectra of the geometrical isomers of $Ni(pic)_3^{2+}$ in aqueous solution at 25°: solid line, purple isomer (*trans*); broken line, brown isomer (*cis*).

TABLE I
THE MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ABSORPTION BANDS OF THE GEOMETRICAL ISOMERS OF TRIS(2-PICOLYLAMINE)NICKEL(II) CHLORIDE DIHYDRATE

Purple isomer		Brown isomer	
λ_{max}, mμ	ϵ, l. mole⁻¹ cm.⁻¹	λ_{max}, mμ	ϵ, l. mole⁻¹ cm.⁻¹
863	8.1	841	13.7
793	7.1	785	13.1
534	9.9		
260	8,600	258	10,900

Since the brown and not the purple isomer is soluble in 2-propanol, it is suggested that the brown form has the more polar *cis* configuration. However, additional basis for the assignment of the isomers may be obtained from three considerations of the absorption spectra. First, it has been found that many *cis* isomers have more intense bands than the corresponding *trans* forms.[4] Figure 1 clearly shows that the brown isomer has the more intense bands. Second, since the *cis* isomer has a cubic symmetry, while the *trans* isomer has a rhombic symmetry,[5] it is expected that the *trans* isomer would have six bands, or at least extensive splitting of the term system electron-transition bands (log $\epsilon \sim 1$).[6] This also agrees with the empirical rule of Linhard and Weigel that the band of longest wave length of the *trans* isomer shows greater splitting than that of the *cis* isomer.[7] Table I indicates the splitting in the longest wave length band of 70 mμ for the purple isomer is greater than the 56 mμ split for the brown isomer. Finally, the spectrum of the purple isomer contains a definite peak at 534 mμ, a third band which Tsuchida reported occurs in all *trans* complexes.[8] However, Basolo found that an ultraviolet band did exist with *cis* compounds, but was invariably found at a shorter wave length than the band for the *trans* isomer, and often obscured by the large ligand–ligand and ligand–metal electron-transition band.[9] The slight shoulder located at about 500 mμ in the spectrum of the brown isomer could be this band. Considering the above evidence, it seems reasonable to assign the *cis* configuration to the brown species and the *trans* structure to the purple species of this complex.

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