Kodak Co., Rochester, N. Y. The white solid melted at 70–72° with decomposition. The following analysis was obtained on this material in our laboratories.

Anal. Calcd. for $C_{27}H_{58}NBr$: C, 68.03; H, 12.27; N, 2.94; Br, 16.77. Found: C, 67.63; H, 12.48; N, 3.01; Br, 16.50.

Tri-*n*-octyl-*n*-propylammonium Aluminohydride (I).—A solution of 47.67 g. (0.10 mole) of tri-*n*-octyl-*n*-propylammonium bromide in 300 ml. of anhydrous benzene was added to a suspension of 5.0 g. of powdered $LiAlH_4$ in 100 ml. of benzene. The mixture was stirred at room temperature for 3 days, after which time a filtered sample of the benzene solution gave a negative halogen test. The suspension was filtered and the filtrate was freeze-dried to yield 21.25 g. of white, crystalline solid, m.p. 61–63° dec. after purification by precipitation from benzene solution with pentane.

Anal. Calcd. for $C_{27}H_{62}NAl$: C, 75.81; H, 14.61; N, 3.27; Al, 6.31. Found: C, 75.51; H, 14.49; N, 3.48; Al, 6.38.

Tetramethylammonium Thiophenoxide (III).—A 10% aqueous solution containing 0.050 mole of tetramethylammonium hydroxide was mixed with 5.51 g. (0.050 mole) of thiophenol and stirred at room temperature until all of the thiophenol had dissolved (approximately 3 days). A small amount of white solid (0.357 g.), which precipitated during the reaction, was isolated by filtration and identified as diphenyl disulfide by its melting point and infrared spectrum. The aqueous filtrate was evaporated to dryness *in vacuo* at 45°, and the resultant off-white solid was dried for 24 hr. at 70° (0.007 mm.) to give 8.98 g. (98% yield) of III. The thiophenoxide melted at 144–145° with decomposition, was extremely hygroscopic, and partially hydrolyzed on standing in moist air as evidenced by the typical odor of thiophenol. The infrared spectrum of III showed no –OH or –SH absorptions.

Anal. Calcd. for $C_{10}H_{17}NS$: C, 65.52; H, 9.35; N, 7.64; S, 17.49. Found: C, 65.80; H, 9.73; N, 8.00; S, 16.80.

Tetramethylammonium Aluminohydride (II).—A suspension of 8.98 g. of III in 110 ml. of THF was mixed with 240 ml. of a 0.233 *M* solution of $LiAlH_4$ in THF and stirred for 2 days at 63°. The suspended solid, which changed from an egg-shell to a bright white color, was isolated by filtration, washed thoroughly with THF, and dried at room temperature *in vacuo* for 5 hr. This procedure afforded 4.52 g. of II (86% over-all yield, based on tetramethylammonium hydroxide). The aluminohydride decomposed above 173° without melting, forming an aluminum mirror in the melting point capillary. It ignited when dropped into water but did not flame in moist air. The density was 0.990 g./cm.^{3} (displacement of *n*-hexane).

Anal. Calcd. for $C_4H_{16}NAl$: C, 45.69; H, 15.34; N, 13.32; Al, 25.65. Found: C, 45.99; H, 15.69; N, 13.01; Al, 25.30; Li, <0.5; S, 0.0.

Results and Discussion

The infrared spectrum of I, taken as a differential in benzene, showed only a simple, relatively sharp, Al–H absorption at 6.03 μ (1660 cm.$^{-1}$). Cryoscopic molecular weight determinations in benzene showed anomalous behavior in that the apparent molecular weight increased with increasing dilution. In tetrahydrofuran (THF), however, ebullioscopic measurements showed decreasing apparent molecular weights with increasing dilution, the values ranging from 12,570 to 285 (5.73% to 0.52% by weight). Isopiestic molecular weight determinations in THF also showed a normal effect of concentration. At 5.33 and 2.66 wt. % concentrations values of 418 and 180, respectively, were obtained. The formula weight of tri-*n*-octyl-*n*-propylammonium aluminohydride is 428.

Tri-*n*-octyl-*n*-propylammonium aluminohydride reacted readily, but not vigorously or completely, with water. Only by incubation in a sealed tube for 2 weeks at 100° with 6 *N* hydrochloric acid could quantitative hydrolysis be effected. A sample of I was heated *in vacuo*, maintained by the continuous pumping of a Toepler pump. No decomposition occurred below 75°; at 90° decomposition was slow. Evolution of hydrogen ceased after several days at 100–109° and the total quantity of hydrogen collected represented 72.4% of the total hydridic hydrogen present in the compound. Another 18.6% was accounted for by the formation of a mixture of condensable gases consisting of 79.5% of *n*-propane and 19.8% of *n*-octane. The residue consisted of metallic aluminum and 95.4% of the theoretical quantity of tri-*n*-octylamine.

Tetramethylammonium aluminohydride (II) was more difficult to prepare than I, since no suitable starting material (soluble in an aprotic solvent) was available. The synthesis was accomplished by using tetramethylammonium thiophenoxide (III), which was found to be slightly soluble in THF. The infrared spectrum of II showed a broad Al–H absorption at 6.03 μ (1660 cm.$^{-1}$) with a shoulder at 5.90 μ (1695 cm.$^{-1}$). Elemental analysis showed that II was quite pure, although it could not be purified by recrystallization because of its insolubility. It was free of sulfur and contained less than 0.5% lithium. The tetramethylammonium aluminohydride was also very difficult to hydrolyze, requiring 14 days of incubation with 6 *N* hydrochloric acid in a sealed tube at 95° to produce 92% of the theoretical quantity of hydrogen.

Both quaternary ammonium aluminohydrides exhibit their principal Al–H absorption near 6 μ in the infrared, suggesting that they exist primarily in the ionic form. This was confirmed in the case of I by preliminary conductivity measurements in THF which showed that the salt had approximately twice the conductivity of $LiAlH_4$ in THF. In the case of II the ionic character of the solid is suggested by its insolubility in organic solvents and its relatively high decomposition temperature. The apparent greater ionic character of these quaternary ammonium aluminohydrides as compared to $LiAlH_4$ may also account for the difficulties encountered in effecting complete hydrolysis.

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The Reaction of Xenon with Dioxygen Difluoride. A New Method for the Synthesis of Xenon Difluoride

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In the course of an investigation of the chemistry of dioxygen difluoride, we have examined its reactivity 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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[2] Single crystal analyses were carried out by W. Hamilton and J. Ibers at Brookhaven National Laboratories.

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

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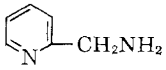
Recently, spectrophotometric studies of some metallic chelates of 2-picolylamine (2-aminomethylpyridine) including the tris chelate of hexacoordinated nickel(II) were reported.[2] However, since 2-picolylamine (pic) is an unsymmetrical ligand being structurally intermediate between ethylenediamine and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

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