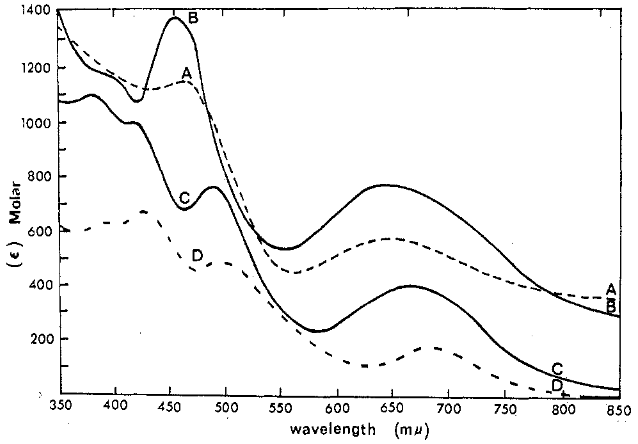

Figure 2.—Absorption spectra of $CoX_2[(CH_3)_2NPF_2]_3$ complexes: (A) $CoBr_2[(CH_3)_2NPF_2]_3$, mull, absorbance in arbitrary units; (B) $CoBr_2[(CH_3)_2NPF_2]_3$, solution in CH_2Cl_2 with excess $(CH_3)_2NPF_2$; (C) $CoI_2[(CH_3)_2NPF_2]_3$, solution in CH_2Cl_2 with excess $(CH_3)_2NPF_2$; (D) $CoI_2[(CH_3)_2NPF_2]_3$, mull, absorbance in arbitrary units.

TABLE II

SPECTRAL DATA FOR $CoX_2[(CH_3)_2NPF_2]_3$ COMPLEXES

X	Solvent	λ (ε)[a]			
I	CH_2Cl_2[b]	26,109 (1100)	23,697 (1000)	20,408 (750)	14,881 (400)
I	Mull	25,773	23,202	19,960	14,706
Br	CH_2Cl_2[b]	25,510 sh (1170)	21,692 (1370)	[d]	15,625 (760)
Br	Mull	25,000 sh	21,739 sh		15,385

[a] Wavelength in cm^{-1}. [b] Excess $(CH_3)_2NPF_2$ added. [c] sh = shoulder. [d] This transition is not observed.

coordinate structure. Other five coordinate low-spin Co(II) complexes exhibit absorptions similar to those which are observed for $CoI_2[(CH_3)_2NPF_2]_3$ and $CoBr_2[(CH_3)_2NPF_2]_3$.[14-17] The true geometry of these pentacoordinate complexes probably is intermediate between trigonal-bipyramidal and square-pyramidal configurations.

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Laser Raman Spectrum of Tetrafluoronitrogen(V) Hexafluoroarsenate(V)

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The preparation[1-4] and the vibrational spectrum[5] of $NF_4^+AsF_6^-$ have previously been reported. It was shown that the NF_4^+ cation is tetrahedral.[1-5] Out of the four fundamental vibrations of NF_4^+, the A_1 and the E mode can be observed only in the Raman spectrum. At the time of the previous spectroscopic study,[5] only a very small amount of material and no laser Raman spectrometer were available to us. The observed infrared spectrum was of very good quality; however, owing to a low signal to noise ratio in the Raman spectrum, only tentative assignments could be made at that time for the A_1 and the E mode.

In this note, we wish to report the laser Raman spectrum of $NF_4^+AsF_6^-$ (see Figure 1, trace A). It is shown that ν_1 (A_1) and ν_2 (E) of NF_4^+ occur at 847 and 445 cm^{-1}, respectively. The value of 847 cm^{-1} for ν_1 (A_1) is close to those of 844 and 836 cm^{-1} deduced from the infrared-active[5] combination bands ($\nu_1 + \nu_4$) and ($\nu_1 + \nu_3$), respectively. The symmetry force constants computed with these revised Raman frequencies are $F_{11} = 8.03$ and $F_{22} = 0.74$ mdyn/Å. Adopting for the F_2 block the previously reported values,[5] the internal force constants of NF_4^+ can be calculated (see Table I). These force constants are not unique since in the F_2 block, three force constants had to be computed from two vibrational frequencies using the approximating method of Fadini.[6] For the isoelectronic species, CF_4 and BF_4^-, this method has yielded values close to those of the general valence force field and, hence, may also be a good approximation for NF_4^+. A detailed discussion of the trends observed within this isoelectronic series has previously been given.[5]

TABLE I

FORCE CONSTANTS OF THE ISOELECTRONIC SERIES NF_4^+, CF_4, BF_4^- (MDYN/Å)

	NF_4^+	CF_4[a]	BF_4^-[a]
f_r	6.22	6.93	4.87
f_{rr}	0.60	0.77	0.62
$f_\alpha - f_{\alpha\alpha'}$	0.98	1.02	0.72
$f_{\alpha\alpha} - f_{\alpha\alpha'}$	0.12	0.16	0.13
$f_{r\alpha} - f_{r\alpha'}$	0.77	0.57	0.43

[a] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer-Verlag, Berlin, 1966, p 69.

The sample used for the present investigation was prepared by the high pressure–temperature method.[4] However, contrary to previous reports,[4] the reaction product was not homogeneous. At the bottom of the Monel reactor, a white, loose solid had accumulated which, according to its elemental analysis, had the approximate composition (in mol %) 93.2 $NF_4^+AsF_6^-$, 5.8 $Ni(AsF_6)_2$, and 1.0 $Cu(AsF_6)_2$. Its vibrational spectrum is depicted by traces A in Figures 1 and 2 and shows the bands expected for the tetrahedral NF_4^+ and the approximately octahedral AsF_6^- ion. About an equal amount of solid product was uniformly distributed over the walls of the reactor. It was pale yellow and, according to its elemental analysis, showed a substantially increased Ni and Cu content. Furthermore, its infrared and Raman spectra (traces B in Figures 1 and 2) show that the bands which in traces A could not be accounted for in terms of octahedral AsF_6^- and tetrahedral NF_4^+ have strongly increased in relative intensity. Therefore, these additional bands must be at-

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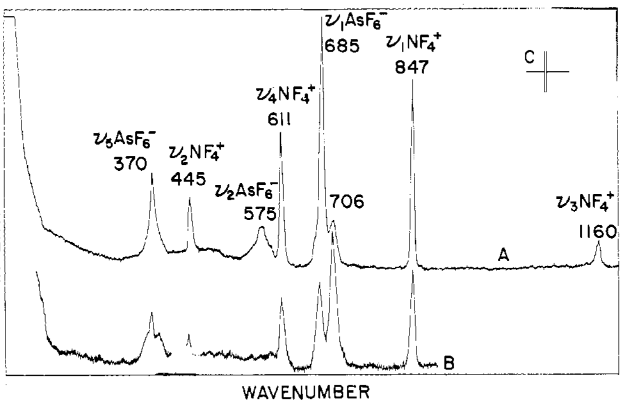

Figure 1.—Replotted Raman spectra of solid $NF_4^+AsF_6^-$ containing smaller (sample I, trace A) and larger (sample II, trace B) amounts of metal salts. C indicates spectral slit width.

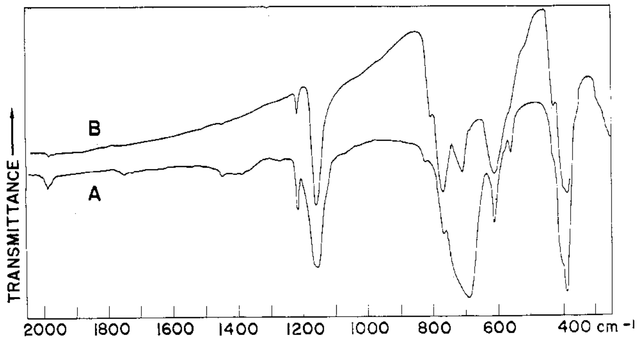

Figure 2.—Infrared spectra of solid $NF_4^+AsF_6^-$. Samples of traces A (AgBr pellet) and B (dry powder between AgCl plates) are identical with those of Figure 1.

tributed to the presence of the metal salts.[7] Furthermore, the previous reports[4] on the hydrolysis of NF_4^+ were confirmed in that NF_3 and O_2 were quantitatively evolved in a 2:1 mole ratio, and no evidence for the formation of nitrogen oxides or oxyfluorides[3] was found.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 IF4Y). Pressures were measured with a Heise-Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitrogen trifluoride (Air Products) and AsF_5 (Ozark Mahoning Co.) were purified by fractional condensation. Prior to its use, fluorine (Rocketdyne) was passed through a NaF trap to remove HF impurities. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box. The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer as dry powders between AgCl or AgBr windows or in the form of pressed AgBr disks. The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to −25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or melting point capillaries were used as sample containers.

Preparation of $NF_4^+AsF_6^-$.—Nitrogen trifluoride (180 mmol), AsF_5 (180 mmol), and F_2 (360 mmol) were heated in a passivated 150-ml Monel cylinder under autogenous pressure to 125° for 20 days. After removal of unreacted starting materials, the cylinder was opened in the glove box and contained about 2.88 g of a solid. About half of the solid had accumulated as a loose white powder (I) at the bottom of the reactor, the rest being distributed in the form of a yellowish layer (II) over the walls of the reactor. *Anal.* Calcd for 93.2 mol % of NF_4AsF_6, 5.8 mol % of $Ni(AsF_6)_2$, and 1.0 mol % of $Cu(AsF_6)_2$: N, 4.50; Ni, 1.21; Cu, 0.22; As, 27.50; total F, 66.59; hydrolyzable F, 6.11; NF_3:O_2 mole ratio, 2.0:1. Found for I: N, 4.64; Ni, 1.21; Cu, 0.23; As, 28.9; total F, 65; hydrolyzable F, 6.2; NF_3:O_2, 2.0:1. Found for II: N, 2.14; Ni, 2.95; Cu, 2.37; As, 28.0; NF_3:O_2, 2.02:1.

Elemental Analysis.—For N, Ni, Cu, As, and hydrolyzable F analyses, a weighted sample was hydrolyzed in a Teflon FEF U trap. The total amount of gas (NF_3 + O_2) was measured volumetrically; then NF_3 was separated from O_2 by fractional condensation at −210°, measured, and identified by infrared spectroscopy. The aqueous solution was analyzed for Ni, Cu, and As by atomic absorption, for As by X-ray fluorescence spectroscopy, and for hydrolyzable F both by $Th(NO_3)_4$ titration and by means of a fluoride electrode. For the total fluoride determination, the sample was fused prior to the F^- analysis using the Parr bomb technique (Na_2O_2 + starch).

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[7] Since the elemental analysis of the Ni- and Cu-rich sample showed an As content somewhat higher than that expected on the basis of the found N, Ni, and Cu values, we have explored the possible presence of a stable $As_2F_{11}^-$ anion in more detail. Solutions of the salt in HF showed only the ^{19}F nmr lines characteristic for NF_4^+, AsF_6^-, and HF, but no evidence for those previously reported (P. A. W. Dean, R. J. Gillespie, and R. Hulme, *Chem. Commun.*, 990 (1969)) for $As_2F_{11}^-$. When CH_3CN was used as a solvent, interaction with NF_4^+ occurred, resulting in a disappearance of the NF_4^+ signals but in a preservation of the AsF_6^- lines. Again no evidence for the $As_2F_{11}^-$ lines was obtained. Attempts to prepare $Cs^+As_2F_{11}^-$ under conditions similar to those used in the $NF_4^+AsF_6^-$ synthesis, *i.e.*, elevated temperature and pressure, produced exclusively $Cs^+AsF_6^-$. On the basis of these findings and the previously reported instability of $As_2F_{11}^-$ salts (P. A. W. Dean, *et al.*, *Chem. Commun.*, 990 (1969)), the presence of a stable $As_2F_{11}^-$ salt in our sample appears unlikely.

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Cobalt(II) Complexes of the Free-Radical Ligand Di-*tert*-butyl Nitroxide

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In view of the interest in stable free radicals as spin labels and because of the potential insight about coordination of O_2 that could be gained by investigating free-radical ligands, we have become interested in the Lewis base di-*tert*-butyl nitroxide.[1] During the course of attempting to prepare various transition metal complexes of the ligand di-*tert*-butyl nitroxide[1] (DTBNO), $[(CH_3)_3C]_2NO$, a stable free radical, we felt it would be worthwhile to reinvestigate the properties of a previously reported compound $Co(DTBNO)_2Br_2$.[2] This complex is prepared quite easily by treating anhydrous $CoBr_2$ with neat DTBNO at room temperature and precipitating out the complex with petroleum ether (bp 30–60°). From elemental analysis and ultraviolet-visible spectroscopy, the compound resembled a conventional four-coordinate pseudotetrahedral cobalt(II) complex and the question immediately arose as to what the magnetic properties of this compound were. When $Co(DTBNO)_2Br_2$ was originally prepared, the room-

[1] This compound was prepared using a variation of the previously reported synthesis by A. K. Hoffmann, *et al.*, *J. Amer. Chem. Soc.*, **86**, 639 (1964). The donor properties toward hydrogen-bonding acids have been described by Y. Y. Lim and R. S. Drago, *ibid.*, **93**, 891 (1971).

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