TABLE III

FAR-INFRARED ABSORPTION BANDS FOR THE METAL NITRATE–PYRIDINE COMPLEXES

Compd	Freq,[a] cm^{-1}		
	ν(M–O)	ν(M–N)	Other bands
$Zn(py)_3(NO_3)_2$	210 s, b[b]	200 s, b[b]	150 w
$Cd(py)_3(NO_3)_2$	190 s[c]	160 s, b[c]	100 w, 72 w, b
$Zn(py)_2(NO_3)_2$	305 s, sp, 285 s, sp	250 w, b, 210 s, b	160 m, b, 90–130 m, b
$Hg(py)_2(NO_3)_2$	303 w, 248 w	220 w, 165 m	130 s, b, 110 s, b
$Cd_2(py)_3(NO_3)_4$	250 m	205 s, b	160 s, b, 90 m, b

[a] Abbreviations used: w, weak; m, medium; s, strong; b, broad; sp, sharp. [b] Broad band between 210 and 200 cm^{-1} which is split into a doublet. [c] Peaks at 160 and 190 cm^{-1} are a broad doublet.

sulfoxide complexes of cadmium nitrate,[13,14] cannot be ruled out. The tris(pyridine)cadmium complex has a molecular weight in excess of 7000 in dimethylformamide, indicating that the complex is polymeric.

The infrared data of the solids are summarized in Tables II and III. The nitrate absorption frequencies show that the nitrate groups are coordinated in these complexes.[15–18] These frequencies are directly comparable to the nitrate frequencies observed for the transition metal pyridine nitrates.[6] The infrared spectrum of coordinated pyridine can be readily distinguished from that of free pyridine by a shift in the strong 1578-cm^{-1} ring vibration band, 8(a), to about 1600 cm^{-1}, and by shifts of the 600- and 400-cm^{-1} bands to about 625 and 420 cm^{-1}, respectively.[19] All pyridines are coordinated in the simple bispyridine and trispyridine complexes, but the trisolvated complexes also show absorption characteristic of uncomplexed pyridine.[20–22] Bands observed in the far-infrared region were tentatively assigned to metal–nitrate (M–O) and metal–pyridine (M–N) stretching modes as indicated. The bands assigned in dinitratotris(pyridine)zinc agree with those of Frank and Rogers,[3] and the metal–oxygen frequencies of dinitratobis(pyridine)zinc agree with those reported by Nuttall and Taylor,[23] who have attributed them to bidentate nitrates, but this assignment has been questioned.[24]

The data do not permit unequivocal assignment of geometries to the complexes. In the trispyridine complexes, the data are consistent with octahedral geometry, with bridging nitrates, similar to the geometry of the transition metal pyridine nitrates. In the bispyridine complexes, the data are consistent with tetrahedral geometry, although other geometries are possible. The cadmium complexes probably have a polymeric, distorted octahedral geometry, with bridging through the nitrate. An X-ray structural study would be advisable for several of these compounds.

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Nickel Fluorochlorates[1a]

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In the reaction of nickel dichloride with fluorine at 150–200°, chlorine monofluoride and chlorine trifluoride are evolved as gaseous products. We have obtained spectral evidence that nickel fluorochlorates, such as $Ni(ClF_2)_2$ and $Ni(ClF_4)_2$, are present in the solid phase at intermediate stages of the reaction. The latter decompose during prolonged fluorination, and the final product is chiefly nickel difluoride. However, the product also contains a small percentage of nickel(III), as shown by its oxidizing power and brown color, which fades rapidly to yellow on exposure to humid air. Infrared bands of the solid indicate that the unstable component is probably a nickel(III) oxyfluoride or acid fluoride.

Experimental Section

Five- to ten-gram amounts of nickel dichloride (Alfa Inorganics, Inc., reagent grade) were dried at 275° in a train with nitrogen and carbon tetrachloride vapor and then were heated to 150–200° in a nickel boat and Monel furnace tube with fluorine (Matheson Chemical Co., 98% purity) at 300 mm pressure. Chlorine fluorides were condensed in a Kel-F trap at $-195°$ on the exit side of the reactor. After approximately 3 hr, the reactor was cooled, evacuated, and filled with dry air, and samples of powder were removed for infrared analysis and tests of oxidizing power. The remaining powder was ground in a drybox, returned to the reactor, and fluorinated again for 3 hr at 1000 mm pressure. This process was repeated until no changes were noted in the spectra with continued fluorination.

Infrared spectra of the dry solids between KBr windows were obtained with a Beckman IR-10 spectrophotometer. (The solids could not be examined as KBr disks or as mulls, since they de-

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(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission; (b) Honors Program Participant, Alfred University; (c) Honors Program Participant, Monmouth College.

composed when ground with KBr powder, mineral oil, or Halocarbon oil in the drybox.) Oxidizing power was determined iodometrically. X-Ray powder patterns of the final product were obtained with a 114.59-mm diameter Philips camera and copper Kα radiation.

Results and Discussion

Figure 1A shows the infrared spectrum from 300 to 1200 cm^{-1} of the solid at the end of the first 3 hr of fluorination. The band at 673 cm^{-1} is ascribed to $Ni(ClF_2)_2$ and the band at 758 cm^{-1} to $Ni(ClF_4)_2$. The difluorochlorate anion, ClF_2^-, absorbs at 635, 636, and 661 cm^{-1} in the compounds $NOClF_2$, $CsClF_2$, and $RbClF_2$, respectively.[2] The tetrafluorochlorate anion, ClF_4^-, absorbs at 742 and 745 cm^{-1} in $CsClF_4$ and $RbClF_4$, respectively.[3] At this stage of fluorination, the solid had an oxidizing power of approximately 0.45 equiv of iodine/mol of nickel. The solid fumed on exposure to air, and the initial brown color faded quickly to pale yellow. Henkel and Klemm[4] obtained a similar product from the fluorination of nickel dichloride, which they considered to be a mixture of NiF_2 and NiF_3 or NiF_4. Although the brown color is indicative of at least a small percentage of nickel(III) in the product at this stage, the oxidizing power and the low nickel content[4] can be more readily ascribed to the presence of ClF_2^- and ClF_4^-.

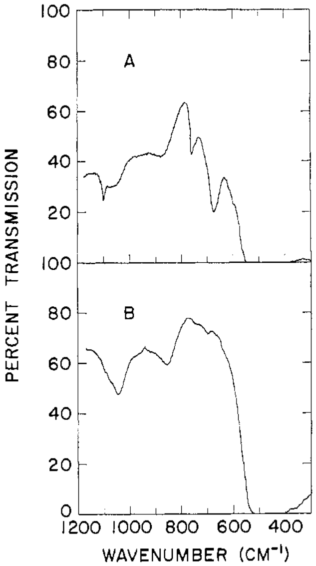

Figure 1.—Infrared spectra of solids obtained from the fluorination of nickel dichloride at 150–200°: (A) product after 3 hr of fluorination; (B) product after 9 hr of fluorination (dry powders).

After 6 hr more of fluorination, the oxidizing power dropped to approximately 0.07 equiv of iodine/mol of nickel, and the solid no longer fumed in air. Broad bands at 855 and 1045 cm^{-1} became more prominent in the infrared spectrum, as shown in Figure 1B, whereas the fluorochlorate bands disappeared. In both Figures 1A and 1B, the major product, nickel difluoride, produced the very strong band from 400 to 550 cm^{-1} (off scale in the figures). The following equations show the formation and decomposition of the transient nickel fluorochlorate compounds

$$NiCl_2 + 2F_2 \longrightarrow Ni(ClF_2)_2$$
$$Ni(ClF_2)_2 + 2F_2 \longrightarrow Ni(ClF_4)_2$$
$$Ni(ClF_2)_2 \longrightarrow NiF_2 + 2ClF$$
$$Ni(ClF_4)_2 \longrightarrow NiF_2 + 2ClF_3$$

The infrared bands at 855 and 1045 cm^{-1} disappeared when the solid was exposed to humid air for several minutes and reappeared when the solid was again fluorinated. X-Ray powder photographs of the solid showed only lines of the major phase, tetragonal nickel difluoride.[5] The compound producing the 855- and 1045-cm^{-1} bands has not been identified thus far. It appears unlikely that this compound is nickel trifluoride, since the frequencies of both bands are too high to be ascribed to nickel–fluorine stretching vibrations. In the complex salts K_3NiF_6 and K_2NiF_6 (which have anions of O_h symmetry), vibration ν_3 occurs at 580 and 663 cm^{-1}, respectively, and in cobalt trifluoride, ν_3 occurs at 565 cm^{-1}. Since stretching vibrations of doubly bound oxygen generally occur in the region 800–1100 cm^{-1} and since bending modes of hydrogen fluoride in acid salts also occur in this region, an unstable oxyfluoride or acid fluoride of nickel(III) is a much more probable source of the two bands.

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The Crystal Structure of Cesium Tetrakis(hexafluoroacetylacetonato)europate and -americate. Isomorphism with the Yttrate[1]

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The publication of a preliminary report on the structure of $CsY(HFA)_4$ (where HFA = hexafluoroacetylacetone) by Lippard, Cotton, and Legzdins[2] led us to extend the study of this type of compound to some lanthanide and transuranic elements[3] and to a complete analysis of the crystal structures[4] of $CsEu(HFA)_4$ and

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