tetragonal Cu(II).[17] This peak is shifted to longer wavelengths as more ligand is added to the solution. When the amount of ligand added is enough to make the ratio of ligand to metal 3 : 1, the spectrum is the same as that of $Cu(PCP)_3(ClO_4)_2$. The spectrum of colorless $Cu(PCP)_3(ClO_4)_2$ in nitromethane solution with a slight excess of PCP shows a peak at 930 mμ (30). This is about the same as is obtained for $Cu(OMPA)_3(ClO_4)_2$ and $Cu(NIPA)_3(ClO_4)_2$.

The infrared data are summarized in Table II. The strong peak in the 1190-cm^{-1} region has been assigned to the P=O stretch since the P=O stretch in $[(CH_3)_2N]_2P(O)CH_3$ was reported as 1205 cm^{-1}.[18] Thomas and Chittenden assigned the frequency range 873–1053 cm^{-1} to be that containing the P—N stretch.[19] The PCH_2P vibration was assigned to the 780–830-cm^{-1} region.[20]

Coordination is believed to be through the phosphoryl oxygen atom with each PCP molecule forming a six-membered chelate ring. This chelate structure has been shown to be correct for OMPA complexes of Co(II), Mg(II), and Cu(II).[6,7] Thus, one would expect and finds much the same changes in the P=O and P—N stretching frequencies in PCP complexes as were found in OMPA and NIPA complexes.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NEW HAMPSHIRE,
DURHAM, NEW HAMPSHIRE 03824

Pyridine Complexes of Zinc, Cadmium, and Mercury(II) Nitrates[1]

BY THOMAS J. OUELLETTE AND HELMUT M. HAENDLER[2]

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Several studies have been made of the pyridine complexes of zinc, cadmium, and mercury(II) halides, but little work has been reported on the pyridine complexes of the corresponding anhydrous nitrates. Frank and Rogers[3] have reported the far-infrared spectrum of dinitratotris(pyridine)zinc(II), and Bullock and Tuck[4] have recorded the infrared spectrum of dinitratobis(pyridine)mercury(II). Pyridine often forms a series of complexes with the same metal salt, as demonstrated with copper(II), cobalt(II), and nickel(II) nitrates,[5,6] and similar behavior might be expected of zinc, cadmium, and mercury(II) nitrates.

Experimental Section

Starting Materials.—Reagent grade methanol was dried by distillation from magnesium activated with iodine. Reagent grade pyridine was dried by distillation from potassium hydroxide and stored over barium oxide. Practical grade 2,2-dimethoxypropane was used without further purification. All other chemicals were of reagent grade and were used without further purification.

Dinitratotris(pyridine)zinc(II).—Granular zinc (7.5 g) was added slowly to a solution of 34 g of silver nitrate in 100 ml of methanol. The mixture was stirred for 32 hr, at which time the solution gave no Ag^+ test. The reaction mixture was filtered and 25 ml of pyridine was added to the filtrate. The mixture was evaporated to a final volume of 40 ml. Colorless, transparent crystals formed on refrigeration and were collected on a sintered-glass filter and washed with methanol and finally with ethyl ether. The product was recrystallized from a chloroform–pyridine mixture and dried *in vacuo* over silica gel. *Anal.* Calcd for $Zn(py)_3(NO_3)_2$: Zn, 15.32; N, 16.42; C, 42.22; H, 3.54. Found: Zn, 15.54; N, 16.41; C, 42.12; H, 3.43.

The compound was also prepared by dehydrating zinc(II) nitrate hexahydrate in 2,2-dimethoxypropane and adding pyridine to the solution at room temperature. It could also be crystallized from methanol–pyridine.

Dinitratobis(pyridine)zinc(II).—A ground and weighed sample of dinitratotris(pyridine)zinc(II) was heated at 115° under a stream of dry nitrogen until no further weight loss was observed (9.5 hr). The final product was a pale pink solid. *Anal.* Calcd for $Zn(py)_2(NO_3)_2$: Zn, 18.81; N, 16.11; C, 34.53; H, 2.88. Found: Zn, 18.98; N, 16.26; C, 34.13; H, 2.86. Calcd weight loss: 18.54%. Found: 18.83%.

Dinitratotris(pyridine)zinc(II)–Tris(pyridine).—A weighed sample of dinitratotris(pyridine)zinc(II) was placed in a desiccator over pyridine for 15 days at room temperature. The starting material added 3 mol of pyridine. The reaction was completely reversible at 60 Torr. *Anal.* Calcd for $Zn(py)_3(NO_3)_2 \cdot 3py$: Zn, 9.85. Found: Zn, 10.29. Microanalytical C, H, and N analyses were not possible because of rapid loss of pyridine from the sample. Calcd weight gain: 55.62%. Found: 54.96%.

Dinitratotris(pyridine)cadmium(II).—An indirect method of oxidizing cadmium in methanol was selected because the oxidation with silver nitrate was very slow, and no Ag^+-free solution could be obtained. Bismuth (15 g) was added to a solution of 34 g of silver nitrate in 100 ml of methanol. The mixture was stirred for 30 hr at room temperature. The mixture was filtered to remove suspended solids, the filtrate giving a negative Ag^+ test. Cadmium filings (12 g) were added to the bismuth(III) solution, and the mixture was stirred for 30 hr and filtered to remove suspended solids. The resulting cadmium nitrate solution gave a negative test for Bi^{3+}. Pyridine (24 ml) was added to the cadmium(II) solution and the mixture was evaporated to a final volume of 40 ml. Colorless, transparent crystals were obtained on refrigeration. These were washed with ether, recrystallized from chloroform–pyridine, and dried *in vacuo*. *Anal.* Calcd for $Cd(py)_3(NO_3)_2$: Cd, 23.72; N, 14.78; C, 38.03; H, 3.19. Found: Cd, 24.18; N, 14.84; C, 37.73; H, 3.10.

The compound was also prepared by dehydrating cadmium(II) nitrate tetrahydrate in 2,2-dimethoxypropane and adding pyridine to the solution at room temperature.

Tetranitratotris(pyridine)dicadmium(II).—A ground and weighed sample of dinitratotris(pyridine)cadmium(II) was heated at 115° under a slow stream of dry nitrogen until no further weight loss was observed (24 hr). The weight loss corresponded to the loss of 1.5 mol of pyridine per mole of starting material.

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[2] To whom communications should be addressed.

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TABLE I

MOLAR CONDUCTANCES OF THE NITRATE COMPLEXES

	Molar conductance, ohm^{-1} cm^2 mole^{-1}, in				
	Methanol	Dimethylformamide			
Compd	10^{-3} *M*	10^{-4} *M*	10^{-3} *M*	10^{-2} *M*	10^{-1} *M*
$Zn(py)_3(NO_3)_2$	164	199	152	90	40
$Zn(py)_2(NO_3)_2$	167	...	...	...	...
$Cd(py)_3(NO_3)_2$	123	165	111	56	23
$Cd_2(py)_3(NO_3)_4$	207	...	...	...	...
$Hg(py)_2(NO_3)_2$	156	170	98	53	24
1:1 electrolytes	100		70–90		
1:2 electrolytes	180		135–175		

Anal. Calcd for $Cd_2(py)_3(NO_3)_4$: Cd, 31.66; N, 13.80. Found: Cd, 31.62; N, 13.85. Calcd weight loss: 25.04%. Found: 24.58%.

Dinitratotris(pyridine)cadmium(II)–Tris(pyridine).—A weighed sample of dinitratotris(pyridine)cadmium(II) was placed in a desiccator over pyridine for 15 days at room temperature. The starting material added 3 mol of pyridine, and the reaction was reversible at 60 Torr. *Anal.* Calcd for $Cd(py)_3(NO_3)_2 \cdot 3py$: Cd, 15.81. Found: Cd, 16.26. No microanalytical C, H, and N analyses were possible because of rapid loss of pyridine from the sample. Calcd weight gain: 50.09%. Found: 49.63%.

TABLE II

INFRARED ABSORPTION DATA FOR METAL NITRATE–PYRIDINE COMPLEXES

	Freq,[a] cm^{-1}, and assignments						
Compd	ν_1, NO$_2$ sym str	ν_2, NO str	ν_4, NO$_2$ asym str	ν_6, nonplanar def	8(a),[b] ring vib	6(a),[b] in plane bend	16(b),[b] out of plane bend
$Zn(py)_3(NO_3)_2$	1300 b	1031	1456	818	1611	634	442, 428[c]
$Cd(py)_3(NO_3)_2$	1280 b	1030	1468	820	1603	632	420, 413[c]
$Hg(py)_2(NO_3)_2$	1305 b	1030	1459	824	1613	658	427, 422[c]
$Zn(py)_2(NO_3)_2$	1300 b	1024	1450	813	1620	648, 635[c]	428, 421
$Cd_2(py)_3(NO_3)_4$	1300 b	1038	1448	820	1612	638, 633[c]	439, 434[c]
$Zn(py)_3(NO_3)_2 \cdot 3py$	1300 b	1029	1459	818	1612	634, 605[d]	421, 403[d]
$Cd(py)_3(NO_3)_2 \cdot 3py$	1280 b	1030	1465	818	1603	632, 607[d]	419, 412,[c] 404[d]
$Hg(py)_2(NO_3)_2 \cdot 3py$	1290 b	1030	1453	819	1610	645, 603[d]	420, 410,[c] 402[d]

[a] Abbreviations used: sym, symmetric; asym, asymmetric; str, stretch; def, deformation; b, broad. [b] Pyridine absorption. [c] Doublet. [d] Peaks from uncoordinated pyridine.

Dinitratobis(pyridine)mercury(II).—This compound was prepared according to the method of Bullock and Tuck.[4] The product was recrystallized from a methanol–pyridine mixture. *Anal.* Calcd for $Hg(py)_2(NO_3)_2$: Hg, 41.54; N, 11.61; C, 24.87; H, 2.09. Found: Hg, 41.46; N, 11.56; C, 24.86; H, 2.04.

A weighed sample of dinitratobis(pyridine)mercury(II) was placed in a desiccator over pyridine for 15 days at room temperature. The starting material added approximately 3 mol of pyridine, but the stoichiometry was not completely reproducible.

Analyses.—Zinc and mercury(II) were determined by standard EDTA titrations with Eriochrome Black T as the indicator, and cadmium was determined by EDTA titration with PAN indicator.[7] The carbon–hydrogen–nitrogen analyses were done by Ingo Hartmann with an F & M Corp. Model 185 analyzer.

Thermal Analyses.—Differential thermal analyses were made with a Fisher Scientific Co. thermal analyzer, at heating rates of 10°/min. Thermogravimetric analyses were done in a nitrogen atmosphere using a thermobalance constructed by Kingston,[8] based on a model described by Wendlandt.[9]

Magnetic Susceptibilities.—Magnetic moments, μ_{eff}, of the solids were determined at 25° by the Gouy method. All samples were diamagnetic.

Conductivity Measurements.—Molar conductances were measured at 25° using a conventional Wheatstone bridge circuit with a cell designed for high-resistance systems. Conductances were determined as a function of concentration in methanol and in dimethylformamide solutions. The compounds were not sufficiently soluble in nitromethane to permit use of this solvent.

Infrared Spectra.—Spectra in the 4000–400-cm^{-1} range were obtained with Nujol and Halocarbon mulls on potassium bromide plates using a Beckman IR-12 spectrophotometer. Those in the 400–33-cm^{-1} range were obtained with Nujol mulls on polyethylene plates, using a Beckman IR-11 spectrophotometer.

Results and Discussion

Dinitratotris(pyridine)zinc and dinitratotris(pyridine)cadmium add 3 mol of pyridine at room temperature to yield the corresponding hexakispyridine complexes. The additions are readily reversible under reduced pressure as confirmed by X-ray diffraction and weight change measurements. Thermal analyses of dinitratotris(pyridine)zinc indicated the formation of only one stable decomposition product, dinitratobis(pyridine)zinc, shown as a strong endothermic peak (121°) on the dta curve. The compound was subsequently synthesized at 115°, following thermogravimetric analysis. A strong exothermic peak above 300° and X-ray analysis indicated final decomposition to zinc oxide. Comparable thermal analyses of dinitratotris(pyridine)cadmium led to isolation of tetranitratotris(pyridine)dicadmium at 115°. There was an indication of formation of another intermediate shortly before decomposition to cadmium oxide, but this could not be isolated. No stable intermediates could be isolated during the thermal decomposition of dinitratobis(pyridine)mercury(II), which was rapid above 180°, leaving mercury as one product.

The conductance data in methanol and in dimethylformamide (Table I) show that the compounds behave as weak electrolytes in these solutions. Comparisons were based on conductance values reported for typical 1:1 and 1:2 electrolytes in dimethylformamide[10] and methanol.[11,12] The values at high concentrations indicate that the compounds are probably nonelectrolytes, with appreciable solvation, although the existence of tetranitrato complexes, such as $[Zn(py)_6][Zn(NO_3)_4]$, similar to those suggested by Addison for dimethyl

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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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CONTRIBUTION FROM THE CHEMISTRY DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS 60439

Nickel Fluorochlorates[1a]

BY LAWRENCE STEIN, JOHN M. NEIL,[1b]
AND GREGORY R. ALMS[1c]

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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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