TABLE I

SPECTRAL DATA FOR $Co(L\text{-hist})_2 \cdot H_2O$

Polarizn of electric vector	ν_{max}(80°K),[a] kK	Excited state	Allowing vibration
$x(b)$	*10.0*	$^4A_1(^4T_{2g}(^4F))$	
	19.3	$^2A_2(^2T_{2g}(^2G))$	
	19.6	$^2A_2(^2T_{2g}(^2G) + \nu$	
	19.8	$^2A_2(^2T_{2g}(^2G) + 2\nu$	
	20.8	$^4A_2(^4T_{1g}(^4P))$	α_2
	22.4 sh	$^4B_1(^4A_{2g}(^4F))$	β_1
$y(a)$	*10.3*	$^4A_2$	
	13.0	$^2A_2(^2T_{1g}(^2G))$	
	16.1	$^2A_2(^2T_{2g}(^2G))$	
	18.7 sh	$^4B_1(^4T_{1g}(^4P))$	β_2
	19.3	$^2A_2$	
	19.6	$^2A_2 + \nu$	
	19.8	$^2A_2 + 2\nu$	
	20.8	$^4A_2$	
	22.3	$^4B_1$	β_2
$z(c)$	11.4	$^4B_2$(?)	
	18.7	$^4B_1$	
	20.8 sh	$^4A_2$	β_2
	22.4	$^4B_1$	

[a] Numbers in italics indicate major spin-allowed, symmetry-allowed bands; sh = shoulder.

In this work we have illustrated how polarized crystal spectra may be used in conjunction with circular dichroism to assign spectral transitions in low-symmetry complexes of cobalt(II). Further spectral and magnetic work is in progress in our laboratory on other cobalt(II)–histidine complexes which will be reported at a later date.

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation (No. GP8756) for the purchase of the JASCO ORD-CD-UV-5 instrument and from the Duke University Biomedical Sciences Support Grant for purchase of the Cary 1402. P. L. M. acknowledges also fellowships from the Shell Oil Co. The authors thank Professor M. M. Harding for the availability of crystallographic results prior to publication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHEASTERN UNIVERSITY, BOSTON, MASSACHUSETTS 02115

Preparation of Pure Difluorophosphoric Acid and μ-Oxo-bis(phosphoryl difluoride)

BY PETER A. BERNSTEIN, FREDERICK A. HOHORST,
MAX EISENBERG, AND DARRYL D. DESMARTEAU*

Received November 9, 1970

Free difluorophosphoric acid, $HOPOF_2$, was first observed by Tarbutton[1] and was later prepared by Lange.[2] Various laboratory methods for the preparation of $HOPOF_2$ are available[3] but since the acid is sold commercially, few investigators would choose to make it. The acid is made commercially by reaction of HF with P_4O_{10},[4] and the product is usually quite impure as received from various suppliers. Purification of the acid by distillation is difficult and we have found that treatment of the impure acid with excess P_4O_{10} at 0° offers a convenient one-step purification.

μ-Oxo-bis(phosphoryl difluoride), $P_2O_3F_4$, the anhydride of $HOPOF_2$ was first isolated by Wannagat[5] from the reaction of PF_3 and O_2 in an electrical discharge. Later, Robinson[6] prepared the compound by dehydration of $HOPOF_2$ with P_4O_{10}. The latter method while easy to carry out always gives a product contaminated with $HOPOF_2$. Fractional distillation gives a reasonably pure product but complete separation from $HOPOF_2$ is very difficult. We have found that $P_2O_3F_4$ can be obtained pure in high yield from the photolysis of POF_2Br with excess oxygen. The POF_2Br is in turn readily obtained pure from the reaction of $HOPOF_2$ with PBr_5.[7]

Experimental Section

General Information.—All manipulations of volatile compounds were carried out in a Pyrex vacuum system equipped with glass–Teflon valves. Pressures were measured using a Wallace and Tiernan differential pressure gauge. The vapor pressure of $HOPOF_2$ was obtained by the method of Kellogg and Cady[8] and that of $P_2O_3F_4$ was obtained by a static method employing the isoteniscope principle.[9]

Infrared spectra were obtained on a Beckman IR10 using a 10-cm glass cell fitted with silver chloride windows. Fluorine nmr were taken on a Varian A-56-60 using $CFCl_3$ as an external reference. Proton nmr were obtained on a Varian A-60 using tetramethylsilane as an external reference.

Reagents.—Difluorophosphoric acid was obtained from Alfa Inorganics. All other materials were reagent grade and were used without further purification.

Purification of $HOPOF_2$.—Impure difluorophosphoric acid (86 g) was cooled to 0° and added to P_4O_{10} (38 g) in a 250-ml bulb cooled in an ice bath. The mixture was allowed to stand for 1 hr at 0° with intermittent shaking. Pure $HOPOF_2$ was then collected by pumping on the mixture held at 0° through a $-78°$ trap. After several hours 32 g of $HOPOF_2$ was collected corresponding to a 37% yield; bp 116.5°; mp -93.1 to $-91.8°$; mol wt 270, calcd mol wt 101.97; nmr: δ 86.2 (d, P*F*), δ -13.3 (s, P–O*H*), $J_{PF} = +992$ Hz; $\Delta H_{vap} = 7.51$ kcal/mol; $\Delta S_{vap} =$ 19.3 eu. Values of the vapor pressure as a function of temperature are as follows [P (mm), t°C]: 20.1, 17.0; 41.0, 30.4; 55.5, 37.2; 101.7, 52.2; 213.9, 72.4; 301.6, 83.4; 342.3, 87.6; 405.5, 93.2; 502.3, 100.4. The data follow the equation

$$\log [P \text{ (mm)}] = 6.1324 - 891.69/T - 14622/T^2$$

The material passing through a $-78°$ trap was found by infrared analysis to contain POF_3 and small amounts of $HOPOF_2$ and SiF_4. The material remaining in the bulb was a very viscous liquid and no effort was made to identify any of the products present.

Preparation of $P_2O_3F_4$.—μ-Oxo-bis(phosphoryl difluoride) was prepared by photolysis of POF_2Br with excess O_2 using an immersion lamp with a 2.5-W output at 2537 Å. Difluorophosphoryl bromide was prepared by the reaction of $HOPOF_2$ (29.0 mmol), PBr_3 (29.5 mmol), and Br_2 (29.7 mmol) in a 250-ml glass bulb for 2 days at 100°. The bulb was fitted with a glass–Teflon valve and was well shielded while being heated. Reactions on a large scale (50 mmol of each reactant) have resulted in occasional breakage of the vessel from the pressure generated by the products. Pure POF_2Br was collected at $-78°$ by pumping the reaction products through a $-40°$ trap. The other products were

---

* Address correspondence to this author at Department of Chemistry, Kansas State University, Manhattan, Kans. 66502.

(1) C. Tarbutton, E. P. Egan, Jr., and S. G. Frary, *J. Amer. Chem. Soc.*, **63**, 1782 (1941).

(2) W. Lange and R. Livingston, *ibid.*, **72**, 1280 (1950).

(3) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 187 (1965).

(4) L. C. Mosier and W. E. White, *Ind. Eng. Chem.*, **43**, 246 (1951).

(5) U. Wannagat and R. Rademachers, *Z. Anorg. Allg. Chem.*, **289**, 66 (1957).

(6) E. A. Robinson, *Can. J. Chem.*, **40**, 1725 (1962).

(7) This method for the preparation of POF_2X compounds was first reported by D. D. DesMarteau, Ph.D. Thesis, University of Washington, Seattle, Wash., 1966. A similar but more extensive study was reported by H. W. Roesky, *Chem. Ber.*, **101**, 636 (1968).

(8) K. B. Kellogg and G. H. Cady, *J. Amer. Chem. Soc.*, **70**, 3986 (1948).

(9) A. Smith and A. W. C. Menzies, *ibid.*, **32**, 897 (1910).

$POBr_3$, HBr, and POF_3 and the reaction was essentially quantitative according to the equation

$$HOPOF_2 + PBr_5 \longrightarrow POBr_3 + HBr + POF_2Br$$

In some instances small amounts of Br_2 were present in the POF_2Br. This was readily removed by shaking the POF_2Br for a few minutes with pure mercury. A small excess of PBr_5 is necessary to ensure complete reaction of $HOPOF_2$. The $HOPOF_2$ is difficult to separate completely from POF_2Br whereas excess PBr_5 is easily removed. The purity of POF_2Br was checked by infrared analysis[10] and by vapor density (mol wt: found, 165.0; calcd, 164.85).

In a typical preparation of $P_2O_3F_4$, POF_2Br (4.4 mmol) and O_2 (7.0 mmol) were added to a 550-ml bulb. The bulb fitted with the immersion lamp was predried by heating under high vacuum and treating with $P_2O_3F_4$. The mixture was then photolyzed for 5 hr. The brown color of bromine was evident after a few minutes. Separation of the products was carried out by pumping on the bulb through −78 and 196° traps. The −196° trap contained POF_3 and small amounts of Br_2. The −78° trap contained a mixture of $P_2O_3F_4$ and Br_2. The Br_2 was removed by shaking with dry mercury. The yield of $P_2O_3F_4$ was 2.0 mmol or 85% based on the equation

$$2POF_2Br + 0.5O_2 \xrightarrow{2537\ \text{Å}} P_2O_3F_4 + Br_2$$

An alternative method of purification which results in somewhat lower yields is first to condense out the products in a cold finger on the bulb. The bulb is then evacuated and while pumping on the vessel a −40° bath is placed around the cold finger. Pumping is continued until the brown color of Br_2 is no longer visible. The remaining material is then pure $P_2O_3F_4$. This latter procedure has the advantage that fewer manipulations of $P_2O_3F_4$ are required and there is less chance of contaminating the very water-sensitive compound; bp 70.8°; mp −1.0 to 0.0°; mol wt 186.0, calcd mol wt 185.93; nmr: δ 81.0 (d, m, P*F*), $J_{PF} = 1048$ Hz; $\Delta H_{vap} = 8.58$ kcal/mol; $\Delta S_{vap} = 25.0$ eu. Values of the vapor pressure as a function of temperature are as follows [*P* (mm), *t*°C]: 38.4, 0.0; 57.4, 8.9; 75.9, 15.2; 114.4, 23.1; 150.5, 29.9; 210.4, 37.9; 283.9, 45.1; 338.0, 49.5; 404.2, 54.0; 490.8, 58.9; 595.5, 64.0; 713.1, 69.0. The data follow the equation

$$\log [P(\text{mm})] = 9.9570 - 2991.0/T + 19186/T^2$$

Results and Discussion

The physical properties of $HOPOF_2$ obtained in this work agree fairly well with those reported by Lange[2] but disagree with the more recent data of Russian workers.[11] Values for $P_2O_3F_4$ are more scarce but our results agree reasonably well with those available.[5,6] The infrared spectra of $HOPOF_2$ and $P_2O_3F_4$ are shown in Figures 1 and 2. The spectra are quite similar except for the broad OH absorption in $HOPOF_2$ and the $\nu(P{=}O)$ which occurs at 1330 cm^{-1} in $HOPOF_2$ and 1405 cm^{-1} in $P_2O_3F_4$. The only reported infrared data for $P_2O_3F_4$ give a medium absorption at 1330 cm^{-1} along with other weaker absorptions readily assigned to $HOPOF_2$.[12] Based on our inability to obtain $P_2O_3F_4$ completely free of $HOPOF_2$ by dehydration with P_4O_{10}, the assignments in the vibrational spectrum of $P_2O_3F_4$[6,12] should be reexamined. The observed molecular weight for $HOPOF_2$ indicates considerable association in the vapor phase and the broad, structured ν(OH) in the infrared spectrum of $HOPOF_2$ substantiates this.

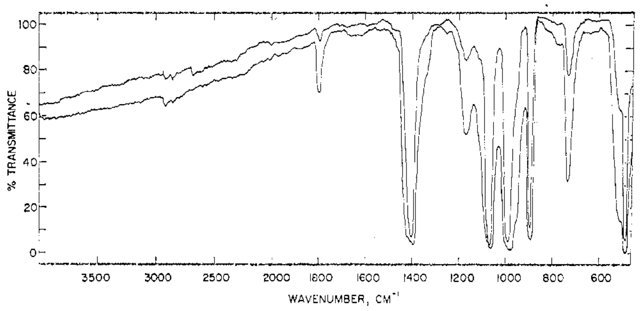

Figure 1.—Infrared spectrum of $P_2O_3F_4$ (4, 26 mm).

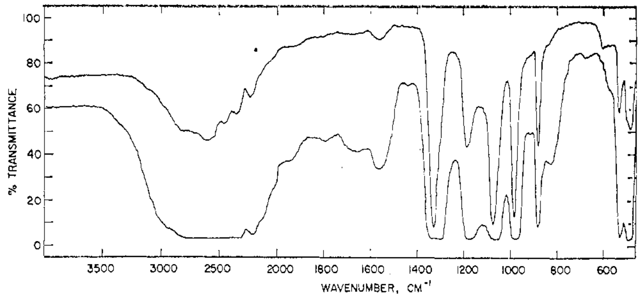

Figure 2.—Infrared spectrum of $HOPOF_2$ (4, 27 mm).

Difluorophosphoric acid purified by our method can be stored for months in glass at 22° without appreciable decomposition. The purity of the acid is supported by the ^{19}F and ^1H nmr as well as the infrared spectrum. No absorptions due to likely impurities such as $(HO)_2POF$, POF_3, $P_2O_3F_4$, or SiF_4 could be observed. Over a 3-month period some POF_3 was formed and after transferring out the $HOPOF_2$ a small amount of a nonvolatile liquid was present. At 100° in glass, $HOPOF_2$ decomposes at a moderate rate to POF_3 and a nonvolatile liquid which is probably $(HO)_2POF$. While we did not study this decomposition quantitatively, the following equation is reasonable for the very small amount of decomposition observed at 22° and the more rapid decomposition at 100°: $2HOPOF_2 \rightarrow POF_3 + (HO)_2POF$. This decomposition does not involve HF or H_2O as almost no SiF_4 is observed. In $HOPOF_2$ samples impure with H_2O and HF, glass attack is rapid and large amounts of SiF_4 are formed. Since $HOPOF_2$ can be prepared from POF_3 and $(HO)_2POF$, the observed decomposition indicates an equilibrium is involved with K_{eq} being very small at 22°: $2HOPOF_2 \rightleftarrows POF_3 + (HO)_2POF$.

The preparation of $P_2O_3F_4$ by photolysis of POF_2Br in the presence of oxygen may involve the formation of POF_2 radicals. Without oxygen the POF_2Br can be recovered essentially unchanged after being photolyzed for several hours. When O_2 is added, Br_2 is formed very rapidly, and if mercury is added instead of oxygen, $P_2O_2F_4$ is formed.[13] It seems reasonable that the same intermediate is involved in both reactions. μ-Oxo-bis(phosphoryl difluoride) was also obtained when POF_2Cl was photolyzed with oxygen. The reaction is, however, much slower with the chloride and useful yields could only be obtained by recycling unreacted POF_2Cl every few hours after removing the $P_2O_3F_4$ formed. Prolonged photolysis of $P_2O_3F_4$ forms POF_3 and a white solid presumed to be $(PO_2F)_n$.[14]

In order to obtain $P_2O_3F_4$ free of $HOPOF_2$, extremely anhydrous conditions are necessary. In our work we

---

(10) Von A. Müller, E. Niecke, and O. Glemser, *Z. Anorg. Allg. Chem.*, **350**, 246 (1967).

(11) A. S. Lenski, A. D. Shaposhnikova, and A. S. Allilueva, *Zh. Prikl. Khim.*, **35**, 760 (1962).

(12) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **9**, 379 (1970).

(13) D. D. DesMarteau, *J. Amer. Chem. Soc.*, **91**, 6211 (1969).

(14) D. W. Muenow, O. M. Uy, and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **31**, 3411 (1969).

found that conditioning of the glass vacuum system with crude $P_2O_3F_4$ obtained from dehydration of $HOPOF_2$ was an effective means of drying the system. Care must also be taken to ensure that POF_2Br is free of any unreacted $HOPOF_2$ or HBr formed in the preparation of POF_2Br because hydrogen bromide reacts readily with $P_2O_3F_4$ to form POF_2Br and $HOPOF_2$. The ^{19}F nmr and infrared spectra and molecular weight of $P_2O_3F_4$ all indicate that the compound can be obtained quite pure by the photolysis of POF_2Br with O_2. The observed ^{19}F nmr spectrum agrees with that reported by Colburn and coworkers for pure $P_2O_3F_4$.[15,16] In agreement with these workers only a two-line spectrum is observed if appreciable $HOPOF_2$ is present.

Acknowledgment.—This work was supported in part by the National Science Foundation (Grants GP-23098 and GP-8892) and by the Petroleum Research Fund of the American Chemical Society (Grant PRF-4563). The authors also thank D. T. Dix and the Dow Chemical Co. for the use of the nmr spectrometer. F. A. H. thanks Goodyear Atomic Corp. for a leave of absence.

[15] W. E. Hill, D. W. A. Sharp, and C. B. Colburn, *J. Chem. Phys.*, **50**, 612 (1969).

[16] These workers obtained the ^{19}F nmr at 40 Mc in $CFCl_3$ and observed a six-line spectrum. At 56.4 Mc using a neat sample we observed further splitting and the question is under study.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH
AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Aquation Equilibrium and Isotopic Exchange of Chloride for Chloro(diethylenetriamine)platinum(II) Chloride[1]

BY JOHN R. PAXSON AND DON S. MARTIN, JR.*[2]

Received December 18, 1970

The concept of the nucleophilicity parameter with its associated nucleophilic discrimination coefficient, since its inception by Belluco, *et al.*,[3] in 1965, has served as an exceedingly useful means for rationalizing trends in the kinetics of ligand substitution reactions for square-planar complexes. In addition, as Basolo, Gray, and Pearson[4] proposed, the rates of chloride or bromide replacements from the $Pt(dien)X^+$ complexes where X is halide and dien is diethylenetriamine are especially informative about trends in entering-group and leaving-group effects. It has been noted that plots of log k_y *vs.* n^0_{Pt} for iodide, bromide, and chloride displacements of the halide in these complexes have given an exceedingly good correlation[5] (see Figure 1) with the exception of the replacement of chloride by chloride. This rate was originally determined by an isotopic exchange procedure in which chloride was separated from the complex by a silver chloride precipitation.[6] Since work in this laboratory has shown that silver chloride precipitates sometimes catalyze the exchange of chloride ligands in platinum(II) complexes, the present study was undertaken to apply an ion-exchange technique for the chloride separation.

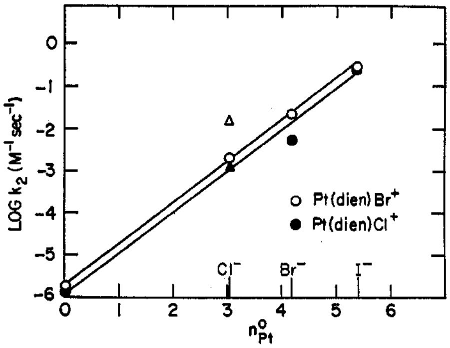

Figure 1.—Dependence of the second-order rate constants (25° and zero ionic strength) for the replacement of Cl^- and Br^- ligands from $Pt(dien)X^+$ upon the nucleophilic reactivity constants of the entering halide nucleophile: △, rate from data of Gray for k_{Cl};[6] ▲, present work.

Experimental Section

The [Pt(dien)Cl]Cl was prepared by the method of Watt.[7] Solutions of LiCl, which served as the source of free chloride and $LiClO_4$ for the control of ionic strength, were prepared from recrystallized reagents. These reagents were required for compatibility with dioxane scintillator solutions used for counting the β rays of ^{36}Cl in a Beckman Liquid Scintillation System, LS 200. In exchange experiments a solution of ^{36}Cl was added to a solution of [Pt(dien)Cl]Cl in LiCl and $LiClO_4$ which had attained equilibrium with respect to the aquation reaction

$$Pt(dien)Cl^+ + H_2O \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} Pt(dien)(H_2O)^{2+} + Cl^- \qquad (1)$$

Exchange was quenched by passing aliquots through a 50-cm exchange column, of 14-mm i.d., containing Amberlite IRA 400 resin in the ClO_4^- form.

The aquo ligand in the product of reaction 1 is a measurably strong acid. However, the equilibrium constant is so small that it has not been possible by manual titration techniques to evaluate the concentration of the aquo complex. However, by using an automatic titrator (Radiometer SBR2c/ABU1c/TTA3) such titrations could be completed in 30 sec and the equilibrium constant has been determined directly.

Results and Discussion

The results of the evaluation of concentrations of $Pt(dien)(H_2O)^{2+}$ by titrations are included in Table I.

TABLE I

AQUATION EQUILIBRIUM FOR $Pt(dien)Cl^+$

Temp, °C	Ionic strength, *M*	$[Pt(dien)Cl^+]$, m*M*	10^4K_s, *M*
25.0	0.100	0.5–5.0	1.96 ± 0.03
25.0	0.318	0.5–5.0	2.52 ± 0.03
35	0.100	0.5–2.5	2.09 ± 0.01
35	0.318	0.5–2.5	2.43 ± 0.04

The values at μ = 0.100 *M* have been used in treating the exchange data. The values at the two ionic strengths are consistent with anticipated behavior of the ionic activity coefficients.[8] The K_s at 0.318 *M* is somewhat lower than the value of 3.7×10^{-4} *M* esti-

---

[1] Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2848.

[2] To whom correspondence should be addressed.

[3] U. Belluco, L. Cattaline, F. Basolo, R. G. Pearson, and A. Turco, *J. Amer. Chem. Soc.*, **87**, 241 (1965).

[4] F. Basolo, H. B. Gray, and R. G. Pearson, *ibid.*, **82**, 4200 (1960).

[5] D. S. Martin, Jr., *Inorg. Chim. Acta Rev.*, **1**, 87 (1967).

[6] H. B. Gray, *J. Amer. Chem. Soc.*, **84**, 1548 (1962).

[7] G. W. Watt and W. A. Cude, *Inorg. Chem.*, **7**, 335 (1968).

[8] C. E. Crouthamel and D. S. Martin, Jr., *J. Amer. Chem. Soc.*, **72**, 1382 (1950).