gether with values of $-\Sigma\sigma^*$, the sum of Taft σ^* constants[7] for the groups (R, R′) present in the thioethers.

Discussion

The spectroscopic and conductance measurements referred to above suggest that the rate constants in Table II refer to reactions 1 and that, with $Y^- = Br^-$ or I^-, these reactions are followed by the much slower processes

$$\mathrm{Pt(bipy)Cl(Y)} + \mathrm{Y}^- \longrightarrow \mathrm{Pt(bipy)Y_2} + \mathrm{Cl}^- \qquad (2)$$

The $-\Sigma\sigma^*$ values are a measure of the inductive effect of R and R′ and it has been shown that they are in linear relationship with the free energy of activation, in processes where thioethers act as entering groups.[4,8]

As one might expect for the attack at these "soft" substrates, the order of nucleophilicity is $I^- > Br^- > Cl^-$. Moreover, there is a linear decrease of the reactivity, expressed in terms of log k_2, as the σ-donor ability of the thioethers, measured in terms of $-\Sigma\sigma^*$, increases. In fact, plots of log k_2 against $-\Sigma\sigma^*$ for each entering group give three parallel straight lines. This indicates that the ability of each substrate to discriminate between the various reagents does not depend upon the nature of the displaceable thioether, and the ability of the entering group to discriminate between the various substrates does not depend upon its own nature. It also indicates that, as might be expected in these reactions, the bond-making and bond-breaking aspects of the substitution can be discussed separately.

In the reactions of the type

$$\mathrm{Pt(bipy)(X)Y} + \mathrm{RSR'} \longrightarrow \mathrm{Pt(bipy)(RSR')Y}^+ + \mathrm{X}^-$$

the effect of the nature of the leaving group on the reaction rate was relatively small (increasing by a factor of 7 on going from $X = N_3$ to $X = Cl$) whereas the effect of the nature of the entering group was significant. In the case of the reactions reported here, the natures of both the entering and leaving groups are of importance. The increase of the reaction rate with the nature of the entering anion is greater than 3 orders of magnitude on going from $Y^- = Cl^-$ to $Y^- = I^-$, and its dependence upon the nature of the displaced thioether is also extremely marked. These facts are consistent with the view that, in these reactions, the second maximum in the reaction profile is of higher energy. If the converse were true, the rate of these asynchronous processes might markedly depend on the degree of bond formation in the activated complex between the metal and the entering group but not on the nature of the leaving group, which would still be strongly bonded to the metal as it was in the ground state. However, if the second maximum is of higher energy, the rate might depend on the degree of bond rupture in the activated complex and therefore upon the nature of the leaving group, as well as on the nature of the entering reagent which becomes firmly bonded to the metal in the activated complex.

A plausible explanation for the behavior of thioethers in these and other reactions[9,10] may be given in terms of a stereoelectronic hindrance arising from interference between the nonbonded lone pairs of electrons on the sulfur and the distribution of charge on the complex. In the case of the entry of thioethers this hindrance arises in the formation of the activated complex and makes bond formation more difficult so that the degree of bond making will be rate determining. When thioethers are the leaving groups, they are present both in the ground and transition states and a relatively higher degree of bond rupture in the activated complex should favor the reaction rate.

Finally, if the rate constants for the forward reactions do not vary significantly with ionic strength, we can combine the present results with those obtained earlier[4] and calculate equilibrium constants for the reactions

$$\mathrm{Pt(bipy)Cl_2} + \mathrm{RSR'} \rightleftarrows \mathrm{Pt(bipy)Cl(RSR')}^+ + \mathrm{Cl}^- \qquad (3)$$

where $R = CH_3$ and $R' = C_6H_5$, CH_3, or C_2H_5.

Assuming that the free energy of the reactants does not depend markedly on the nature of the thioether, the relative free energies of the products may be determined from these three equilibrium constants. The relative free energies of activation may also be calculated from the rate constants reported earlier.[4] A comparison of the total and activation free energies shows that the nature of the thioether affects the ground-state energy of the system $\mathrm{Pt(bipy)Cl(RSR')}^+ + \mathrm{Cl}^-$ to a greater extent than it affects the energy of the transition state. This is in accord with the conclusion that the Pt–S bond is partially broken in passing from the ground state to the transition state for the reverse of (3).

Acknowledgments.—We thank Dr. J. S. Coe and Dr. M. L. Tobe for helpful stimulating discussions. This work has been financially supported by the Italian Council for Research (CNR Rome).

---

[7] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newmann, Ed., Wiley, New York, N. Y., 1965.

[8] L. Cattalini, G. Marangoni, and M. Martelli, *Inorg. Chem.*, **7**, 1495 (1968).

[9] L. Cattalini, G. Marangoni, and M. Martelli, *Proc. Symp. Coord. Chem., 1970*, 347 (1970).

[10] L. Cattalini, G. Marangoni, J. S. Coe, and M. Martelli, *J. Chem. Soc. A*, 593 (1971).

CONTRIBUTION FROM THE
PAUL M. GROSS CHEMICAL LABORATORY,
DUKE UNIVERSITY, DURHAM, NORTH CAROLINA 27706

Circular Dichroism and Polarized Crystal Spectra of Cobalt(II) L-Histidinate Complexes[1]

BY P. L. MEREDITH AND R. A. PALMER*

Received August 24, 1970

The importance of simple transition metal complexes of the essential amino acid histidine as "model" systems for metal-activated enzymes has been discussed previously.[2] Interest in histidine complexes of the cobaltous ion has been particularly widespread stimulated by the reversible oxygen-carrying capacity of cobalt(II)–histidine solutions.[3] Complementing the extensive solution investigations, a few reports of specific solid-state compounds have also been made. Isolation of the oxy-

---

[1] (a) Presented in part at the 155th National Meeting, of the American Chemical Society, San Francisco, Calif., 1968; see Abstracts, No. M124. (b) Taken in part from the Ph.D. thesis of P. L. Meredith, Duke University, 1970.

[2] P. L. Meredith and R. A. Palmer, *Inorg. Chem.*, **10**, 1049 (1971).

[3] J. Z. Hearon and D. Burk, *J. Nat. Cancer Inst.*, **9**, 337 (1949).

genated compound, $[Co(L\text{-}hist)_2]_2 \cdot O_2$, has been reported and its actual structure hypothesized based on infrared spectra,[4] although the instability of its crystals has so far precluded any X-ray work. Crystal structures of D-histidinato-L-histidinatocobalt(II) dihydrate[5] and bis(L-histidinato)cobalt(II) monohydrate[6,7] have been determined. In this communication we report electronic absorption spectra of single crystals of $Co(L\text{-}hist)_2 \cdot H_2O$ in polarized light obtained at ambient and cryogenic temperatures. The spectra have been analyzed and assigned in light of the energies and polarizations of the bands. The circular dichroism spectra of cobalt(II)–L-histidine solutions are also presented as supporting evidence for the band assignments.

Experimental Section

All crystals were grown from aqueous solution. The crystals were grown in a completely deaerated, evacuated, and sealed vessel consisting of two 250-ml Erlenmeyer flasks connected by a 1-in. i.d. sealing tube, which contained a medium-porosity frit midway in its length. The dry solids L-histidine and $CoCO_3$ were added to one side of the vessel (flask A); freshly boiled water was added to flask B. The system was thoroughly degassed on the vacuum line. The water was then transferred into flask A and the reaction was urged to completion with gentle heating and stirring. After pumping off the CO_2 formed, the vessel was sealed and the pale orange-pink solution of the complex was filtered through the frit into flask B. Growth of the crystals was accomplished by very slowly distilling the water back from solution flask B to the reaction flask A using a small temperature differential. The crystals were recovered by filtration from the orange solution in a dry nitrogen atmosphere, washed with 95% ethanol which had been purged with nitrogen, and then stored in a sealed vial. Thus treated the crystals remained stable for over 1 year. The identity of the crystals was verified and the axes were located with respect to the prominent faces by standard X-ray diffraction techniques. The single-crystal absorption spectra were determined on a Cary Model 14R spectrophotometer using techniques described previously.[2]

Solutions for measuring circular dichroism (CD) spectra were prepared in a glove bag after overnight purging of all reagents with nitrogen. That the solutions were free from oxygen was confirmed by the absence of the characteristic broad CD peak of the O_2 complex at 28.2 kK.[8] The pH of solutions was varied by adding small portions of either 0.1 or 1.0 *M* NaOH to the 0.02 *M* solution of the $Co(L\text{-}hist)_2$ complex. CD spectra were measured on a Durrum-Jasco ORD-CD-UV-5 spectropolarimeter and circular dichroism recorder in the visible region and on a Cary 1402 circular dichroism attachment for the Cary 14R spectrophotometer in the near-infrared region.

Results and Discussion

Crystal spectra were measured with light normal to the (201) face (which is generally the largest) and normal to the (100) face, polarized along the extinction directions in both cases. Polarization parallel to the *b* axis was common to both views, while the orthogonal polarization in the (201) view was approximately parallel to the *a* axis and, in the (100) view, parallel to the *c* axis. Inspection of the molecular packing in the crystal[7] reveals the following relationships between the crystal polarizations and the molecular polarizations, assuming an oriented gas model

$$\epsilon_x = \frac{\epsilon_c \cos^2 63° - \epsilon_b \cos^2 27°}{\cos^4 63° - \cos^4 27°}$$

$$\epsilon_z = \frac{\epsilon_c \cos^2 27° - \epsilon_b \cos^2 63°}{\cos^4 27° - \cos^4 63°}$$

$$\epsilon_y = \frac{\epsilon_a - \epsilon_z \cos^2 27° \cos^2 66° - \epsilon_x \cos^2 79°}{\cos^2 24°}$$

where $\epsilon_{a,b,c}$ refer to molar absorptivities in the three distinct crystal polarizations, and $\epsilon_{x,y,z}$, to the molar absorptivities which, according to the model, would be observed if the electric vector were parallel to the *x*, *y*, or *z* molecular axis.

The spectra calculated from measurements at 80°K (Figure 1) reveal two band systems typical of six-coordinate cobalt(II) complexes. The lack of significant temperature dependence of the total intensities of the three different spectra suggest that a triaxial, noncentrosymmetric point group is required for the interpretation. The $Co(L\text{-}hist)_2 \cdot H_2O$ crystal is reported[9] to be isomorphous with that of $Ni(L\text{-}hist)_2 \cdot H_2O$, which shows a spectrum lending itself to interpretation in C_{2v} symmetry.[2] Therefore, it is proposed that the principal intensity-determining factor in the cobalt complex spectrum is also a static C_{2v} field. Although many cobalt(II) complexes have been discussed in terms of O_h symmetry, very few efforts have been made to interpret the spectra of low-symmetry complexes. (Ferguson has successfully interpreted spectra of $Co(py)_2Cl_2$ in D_{2h} symmetry.[10]) The crystal structure of $Co(L\text{-}hist)_2 \cdot H_2O$ has shown that the molecule has an approximate twofold axis of symmetry bisecting the O–Co–O and N_A–Co–N_A angles.[17] This is chosen as the *z* molecular axis. The *y* molecular axis is chosen along the N_I–

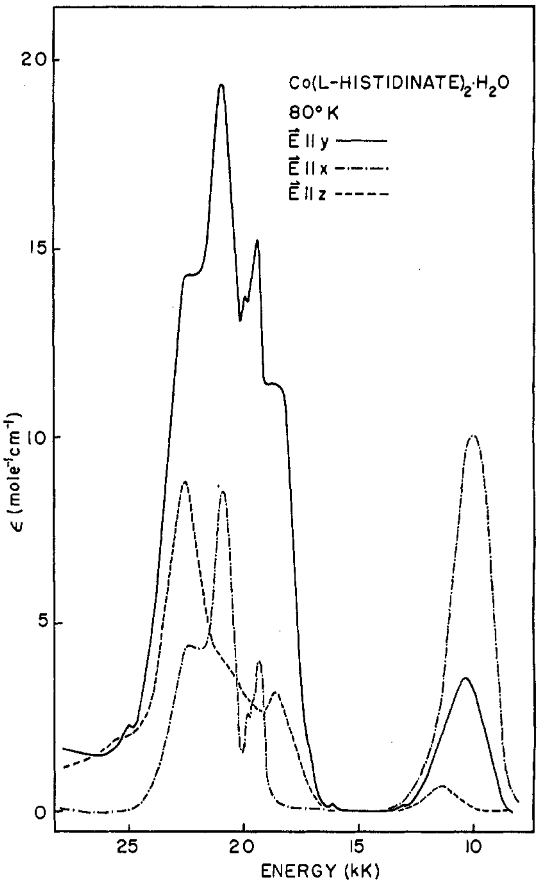

Figure 1.—Molecular spectra of $Co(L\text{-}hist)_2 \cdot H_2O$ calculated from the polarized crystal spectra measured at 80°K.

---

(4) Y. Sano and H. Tanabe, *J. Inorg. Nucl. Chem.*, **25**, 11 (1963).

(5) R. Candlin and M. M. Harding, *J. Chem. Soc. A*, 384 (1970).

(6) K. A. Fraser and M. M. Harding, *Chem. Commun.*, 344 (1965).

(7) M. M. Harding and H. A. Long, *J. Chem. Soc. A*, 2554 (1968).

(8) P. L. Meredith and R. A. Palmer, unpublished observations.

(9) M. M. Harding, private communication.

(10) J. Ferguson, *J. Chem. Phys.*, **32**, 533 (1960).

Co–N_I axis. This is the same assignment of the axes as was used for the nickel analog.[2]

The lowest energy band system in the spectrum lies at 10.0 kK. In terms of the parent O_h symmetry this is the $^4T_{2g}(F) \leftarrow {}^4T_{1g}$ transition. A simple octahedral ligand field calculation including configuration interaction[11] gives a value of $Dq = 1.10$ kK. On this basis also the visible absorption is assigned as due principally to bands related to the $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ transition. This calculation also suggests that the two-electron transition $^4A_{2g}(F) \leftarrow {}^4T_{1g}$ may lie above the $^4T_{1g}(P)$ bands. In a discussion of cobalt(II) spectra, Lever and Ogden[12] showed that, in regular octahedral derivatives, the $^4A_{2g} \leftarrow {}^4T_{1g}$ transition must have an energy at least twice that of the lowest energy transition. Since the lowest energy band lies at 10.0 kK in $Co(L\text{-hist})_2 \cdot H_2O$, the $^4A_{2g} \leftarrow {}^4T_{1g}$ band should be in the 20–22-kK region.

In C_{2v} symmetry all orbital degeneracy is lifted and the substantial splittings observed in the spectrum of $Ni(L\text{-hist})_2 \cdot H_2O$[2] lead to prediction of similar splittings in the cobalt analog. Large splitting of the octahedral ground state ($^4T_{1g}(F)$) should allow population of only one singly degenerate state even at room temperature and produce strong polarizations comparable to those in the nickel complex spectrum. This is, in fact, just what is observed. The order of energies of the one-electron orbitals found for the nickel complex ($z^2 > x^2 - y^2 > xy > (1/\sqrt{2})(xz - yz) > (1/\sqrt{2})(xz + yz)$)[2] leads to an assignment of the ground state of the d^7 cobalt complex as $^4B_1$. The electric dipole selection rules allow transitions to A_1, A_2, and B_1 levels when $\vec{E}$ is parallel to x, y, and z, respectively. Transitions to B_2 levels are forbidden.

The selection rules then predict no intensity in the z polarization of the infrared band and no intensity in the x polarization of the visible band. This prediction is not fulfilled rigorously. Although the polarization in the infrared spectrum is virtually complete, substantial x intensity is observed in the visible manifold. This indicates that, as in the nickel complex spectra, some vibronic intensity must be involved. Nevertheless, relying on the most intense maxima as guides, the following assignments of bands may be made with internal consistency.

In the infrared band the strongest maximum ($x(b)$ polarized) at 10.0 kK can be assigned to the $^4A_1 \leftarrow {}^4B_1$ transition. This is also the lowest energy component of the manifold as predicted by the orbital energy order. The $^4A_2 \leftarrow {}^4B_1$ transition is then at 10.3 kK, allowed electronically in the $y(a)$ polarization. The minute z intensity may indicate the position of the forbidden $^4B_2 \leftarrow {}^4B_1$ band.

In the visible region the highest energy maximum, at 22.4 kK, which is the most intense component of the $z(c)$ polarization, may be assigned to the $^4B_1(^4A_{2g}) \leftarrow {}^4B_1$ transition on the basis of the energy arguments above, as well as on the basis of polarization. The two remaining broad maxima at 18.7 and 20.8 kK must be assigned to transitions related to the $^4T_{1g}(P)$ state. The 20.8-kK maximum is readily assigned to the $^4A_2 \leftarrow {}^4B_1$ component; however the assignment of the 18.7-kK band to the remaining $^4B_1 \leftarrow {}^4B_1$ transition requires an unusually strong vibronic mechanism to account for the y intensity. Nevertheless, other assignments seem less likely and the orbital energy order does predict $^4A_2 > {}^4B_1$ in the $^4T_{1g}(P)$ manifold.

The progression of sharp maxima at 19.3, 19.6, and 19.8 kK has the appearance predicted for bands associated with intraconfigurational transitions and may confidently be assigned to $^2A_2(^2T_{1g}(^2G)) \leftarrow {}^4B_1$ in the $a(y)$ polarization. The x intensity of this band must be vibronic. It is not clear why so little z intensity is observed. Other very weak, intraconfigurational, doublet-associated bands are observed at 13.0, 16.1, and 25 kK and are assigned to $^2T_{2g}$, $^2T_{1g}(^2G)$, and $^2T_{2g}(^2H)$ levels, respectively. All the quartet–quartet and quartet–doublet band assignments are compatible with the predictions of Liehr,[13] allowing for the large splitting of the $^4T_{1g}(P)$ levels.

Turning now to the CD spectra, we find further support for the above assignments. Although the solution absorption spectrum shows no resolution, the solution CD spectrum at the pH at which the crystals were grown (5.2) (Figure 2) reveals two distinct maxima in the visible region at 19.3 and 20.5 kK. No shift in the energies of these maxima is observed as the pH is raised to 9, nor do any other maxima develop in this pH range (in which the only significant species is known to be the bis complex[14]). These maxima correspond exactly to those assigned in the crystal spectrum to the $^4A_2 \leftarrow {}^4B_1$ and $^2T_1 \leftarrow {}^4B_1$ transitions. (A slight temperature shift of the $^4A_2$ band brings it to 20.8 kK at 80°K (Table I).) Conspicuously missing in the CD spectrum are the bands at 18.7 and 22.4 kK assigned in the crystal spectrum to $^4B_1 \leftarrow {}^4B_1$ transitions. This is consistent with the assignment in that $B_1 \leftarrow B_1$ transitions are magnetically forbidden in C_{2v} symmetry. It should be noted then that the visible CD spectrum consists of the spin-forbidden $^2T_1 \leftarrow {}^4B_1$ band and the only one of the three possible spin-allowed bands which is both electric dipole and magnetic dipole allowed, $^4A_2 \leftarrow {}^4B_1$. In the near-infrared region the CD is less well defined owing possibly to the fact that both the $^4A_2 \leftarrow {}^4B_1$ and $^4A_1 \leftarrow {}^4B_1$ transitions are electrically and magnetically allowed.

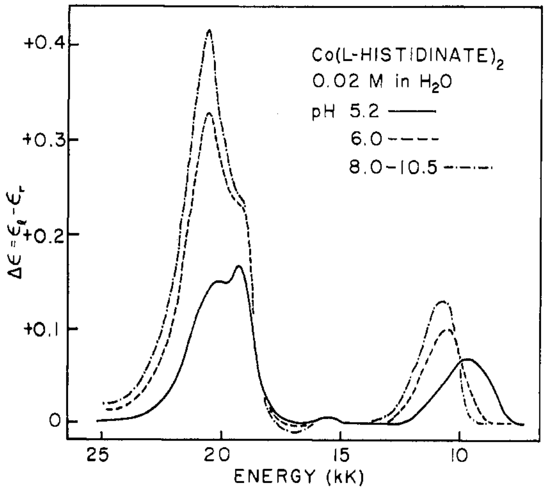

Figure 2.—Circular dichroism spectra of $Co(L\text{-hist})_2$ aqueous solutions.

---

(11) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 256.

(12) A. B. P. Lever and D. Ogden, *J. Chem. Soc. A*, 2041 (1967).

(13) A. D. Liehr, *J. Chem. Phys.*, **67**, 1314 (1963).

(14) P. J. Morris and R. B. Martin, *J. Amer. Chem. Soc.*, **92**, 1543 (1970).

TABLE I

SPECTRAL DATA FOR Co(L-hist)$_2$·H$_2$O

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$_4$O$_{10}$,[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$_4$O$_{10}$ at 0° offers a convenient one-step purification.

μ-Oxo-bis(phosphoryl difluoride), P$_2$O$_3$F$_4$, 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$_4$O$_{10}$. 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$_2$O$_3$F$_4$ can be obtained pure in high yield from the photolysis of POF$_2$Br with excess oxygen. The POF$_2$Br 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$_2$O$_3$F$_4$ 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$_4$O$_{10}$ (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$_2$O$_3$F$_4$.—μ-Oxo-bis(phosphoryl difluoride) was prepared by photolysis of POF$_2$Br 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$_2$Br 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$_2$X 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).