Difluorophosphate Complexes of Chromium, Manganese, Iron, Cobalt, and Nickel†

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The compounds $M(O_2PF_2)_2 \cdot HPO_2F_2$ (M = Mn, Fe, Co, or Ni), $Cr(O_2PF_2)_3 \cdot HPO_2F_2$, and two new forms of $Fe(O_2PF_2)_3$ have been prepared and characterised by elemental analysis, i.r. spectroscopy, magnetic measurements [$M(O_2PF_2)_2 \cdot HPO_2F_2$], and Mössbauer spectroscopy (iron compounds). All the compounds appear to be polymeric with bidentate bridging difluorophosphate groups and the metal atoms in octahedral environments.

Several reviews of difluorophosphoric acid (HPO_2F_2) and difluorophosphates[1-6] have appeared. However, although difluorophosphoric acid is reported to attack most common metals except aluminium, silver, and platinum,[2] the products of reaction of metals with anhydrous difluorophosphoric acid have received scant attention. Here we report the use of reactions of metals with anhydrous difluorophosphoric acid to prepare the novel acid solvates $M(O_2PF_2)_2 \cdot HPO_2F_2$ (M = Mn, Fe, Ni, or Co) and a new form of $Fe(O_2PF_2)_3$. Another new form of $Fe(O_2PF_2)_3$ is available from the reaction of a diethyl ether solution of $FeCl_3$ with HPO_2F_2, and the solvate $Cr(O_2PF_2)_3 \cdot HPO_2F_2$ can be prepared from the reaction of $CrBr_3$ with HPO_2F_2.

Experimental

All the difluorophosphates reported were extremely sensitive to moisture and were handled in an atmosphere of dry nitrogen; $Fe(O_2PF_2)_2 \cdot HPO_2F_2$ was also oxygen-sensitive.

Spectra.—I.r. spectra were recorded for Nujol mulls between caesium iodide (4 000—250 cm^{-1}) and silver chloride (4 000—330 cm^{-1}) windows using a Perkin-Elmer 577 grating spectrometer. Some attack on the caesium iodide windows was observed and so the spectra were checked by also recording them using silver chloride windows. Mössbauer spectra were obtained at 80 K using a Harwell Northern NS-600 spectrometer equipped with a 256-channel analyser using a Pd–^{57}Co source. Calibration of the velocity scale was effected using iron foil. The resultant data were fitted to Lorentzian line shapes by least-squares methods. The isomer shifts quoted are with respect to iron metal. The isomer shifts and quadrupole splittings are considered accurate to at least ± 0.05 and ± 0.10 mm s^{-1} respectively.

Magnetic Measurements.—Room-temperature magnetic moments were determined using the Gouy method, $Hg[Co(NCS)_4]$ being used to calibrate the Gouy tube. No correction for the diamagnetism of the ligands was made but approximate calculations indicated that the effect of the diamagnetic correction on the reported moments was only of the order of 0.05 B.M. The results were reproducible to ± 0.1 B.M.

X-Ray Powder Diffractometry.—Photographs were obtained of finely ground samples loaded into glass capillaries (diameter 0.2, 0.3, or 0.5 mm) in a nitrogen-filled glove-box. The capillary was temporarily sealed with grease, then removed from the glove-box and flame sealed. The powder photographs of iron-containing compounds were obtained using Fe-K_α radiation, filtered by manganese, and those of other compounds using Cu-K_α radiation, filtered by nickel, with a 114.83-mm Debye–Scherrer camera. All the compounds except $Cr(O_2PF_2)_3 \cdot HPO_2F_2$ gave powder photographs. The powder photographs could be used to 'fingerprint' products without the accurate determination of *d* spacings.

Analyses.[7]—Aluminium, manganese, cobalt, and nickel were determined gravimetrically by precipitation from basic solution as the quinolin-8-olates. Iron(II) was determined by titration with standard potassium dichromate solution using $Na[Ph_2NSO_3]$ as indicator. Iron(III) and chromium(III) were determined by atomic absorption spectroscopy using a Perkin-Elmer 603 spectrometer. Iron(III) was also determined gravimetrically as the quinolin-8-olate and chromium titrimetrically with ammonium iron(II) sulphate after oxidation to dichromate. The results were in good agreement with those obtained by absorption spectroscopy.

Phosphorus was determined gravimetrically as ammonium 12-molybdophosphate, $[NH_4]_3[PMo_{12}O_{40}]$. Prior to analysis the products were hydrolysed with 20% nitric acid at 60 °C for 1 h. Interfering fluoride was removed (as fluoroboric acid) by the addition of boric acid.

Fluorine was determined potentiometrically with a lanthanum fluoride-ion-sensitive electrode. Samples were either fused with sodium hydroxide or heated in a sealed container with 10% sodium hydroxide at 120 °C for 24 h prior to analysis. Fluorine could also be isolated as H_2SiF_6 by Willard–Winter distillation from perchloric acid solutions.[8] The results were not completely satisfactory, tending to be slightly low, particularly in the case of $Ni(O_2PF_2)_2 \cdot HPO_2F_2$ (Found: F, 29.0. Requires F, 31.4%) and the form of $Fe(O_2PF_2)_3$ prepared from metallic Fe and HPO_2F_2 (Found: F, 30.0. Requires F, 31.8%). No satisfactory fluorine analysis could be performed on $Cr(O_2PF_2)_3 \cdot HPO_2F_2$.

Materials.—A.R. or commercial grade Mn, Fe, Co, Ni, $FeCl_3$, $FeF_3 \cdot 3H_2O$, $CrBr_3$, and $AlCl_3$ were used without further purification. Commercial difluorophosphoric acid (Ozark Mahoning Chemical Company) was purified by the method of DesMarteau and co-workers.[9] Its purity was established by ^{19}F n.m.r. spectroscopy, using a Bruker WM 250 pulse Fourier-transform spectrometer, observation of only the HPO_2F_2 doublet being the acceptable criterion. Commercial diethyl ether was dried by refluxing over P_2O_5 and distilled before use.

Preparation of Compounds.—(*a*) *Metal–*HPO_2F_2 *reactions.* A quantity of metal (typically 0.5—1.0 g) was placed in a pre-weighed Schlenk tube containing a Teflon-coated stirring bar.

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† *Non-S.I. unit employed:* B.M. ≈ 9.27×10^{-24} A m^2.

An excess of HPO_2F_2 (5—10 times that required for a *metal*:HPO_2F_2 mole ratio of 1:3) was then distilled on to the metal under static vacuum. The reaction vessel was warmed to room temperature, vented *via* a P_2O_5 guard tube, and the mixture stirred magnetically until all the metal had dissolved. The solution was then evacuated to dryness. The weight change of the Schlenk tube enabled the reaction stoicheiometry to be determined as 1:3 (when M = Mn, Co, or Ni) according to equation (1).

$$M + 3HPO_2F_2 \longrightarrow M(O_2PF_2)_2{\cdot}HPO_2F_2 + H_2 \quad (1)$$

Reaction between the metal and the acid was vigorous in all cases and complete dissolution of manganese, cobalt, and nickel was observed after a few hours. Rigorous exclusion of air (*i.e.* oxygen) was found to be necessary in the reaction involving iron in order to obtain an iron(II) product. The reaction was therefore carried out in a specially designed two-limbed vessel incorporating a sinter. The use of this vessel enabled the reaction to be conducted and the solution filtered under oxygen-free conditions. Hydrogen was removed periodically by attaching the vessel to a vacuum system. Under these conditions the reaction did not proceed smoothly to completion and a final filtration stage was invariably necessary to remove unreacted iron metal. The analytical results for the $M(O_2PF_2)_2{\cdot}HPO_2F_2$ series are presented in Table 1.

When the iron–difluorophosphoric acid reaction was carried out in the presence of dry air, a white solid insoluble in HPO_2F_2 was deposited and the acid acquired a pink colour (in contrast to the reaction in the absence of air where the product is highly soluble in HPO_2F_2 and forms a colourless solution). The white solid was isolated by inert-atmosphere filtration and dried in vacuum. Analysis (Found: F, 30.0; Fe, 15.5; P, 25.9%) and Mössbauer spectroscopy, which demonstrated the presence of Fe^{III} only, indicated that the product was a new form of $Fe(O_2PF_2)_3$ (Requires F, 31.8; Fe, 15.6; P, 25.9%). The i.r. (Table 2) and Mössbauer spectra (Table 3) were different from those of the previously reported form of $Fe(O_2PF_2)_3$.[10] This new form of $Fe(O_2PF_2)_3$ also gave a well defined *X*-ray powder pattern unlike the previously reported form which was found to be amorphous to *X*-rays.

Table 1. Analytical data (%) for $M(O_2PF_2)_2{\cdot}HPO_2F_2$ compounds

		Metal		P		F	
Metal	Colour	Found	Calc.	Found	Calc.	Found	Calc.
Mn	White	15.5	15.3	26.1	25.9	30.6	31.8
Fe	White	15.5	15.5	25.5	25.8	30.8	31.7
Co	Red-purple	16.2	16.2	25.6	25.6	30.7	31.4
Ni	Yellow	16.3	16.2	25.4	25.6	29.0*	31.4

* See Experimental section.

(*b*) $CrBr_3$–HPO_2F_2. Difluorophosphoric acid was distilled onto $CrBr_3$ using the same method and apparatus as for the preparation of $M(O_2PF_2)_2{\cdot}HPO_2F_2$ (M = Mn, Co, or Ni). As the reaction proceeded a dark green viscous solution formed. Even in the presence of a considerable excess of difluorophosphoric acid some solid unreacted $CrBr_3$ remained. This was removed by filtration under argon. Excess of HPO_2F_2 was then removed in vacuum producing, on prolonged evacuation, an emerald-green glass which could be ground into an emerald-green powder containing no bromide. Chromium and P analyses corresponded to the formulation $Cr(O_2PF_2)_3{\cdot}HPO_2F_2$ [Found: Cr, 11.7; P, 27.6. $Cr(O_2PF_2)_3{\cdot}HPO_2F_2$ requires Cr, 11.4; P, 27.1%]. The reaction can thus be represented as in equation (2). The compound was found to be virtually insoluble

$$CrBr_3 + 4HPO_2F_2 \longrightarrow Cr(O_2PF_2)_3{\cdot}HPO_2F_2 + 3HBr \quad (2)$$

in all solvents tried, even concentrated mineral acids. It did, however, dissolve in aqueous perchloric and nitric acids on prolonged heating.

(*c*) $FeCl_3$–Et_2O–HPO_2F_2. A saturated solution of $FeCl_3$ in diethyl ether was placed in a Schlenk vessel. A ten-fold excess of difluorophosphoric acid was then vacuum distilled into the vessel, which was vented *via* a P_2O_5 guard tube and stirred magnetically. The white powder which separated was isolated by filtration, washed with diethyl ether, and dried in vacuum. The product was identified as a second new form of $Fe(O_2PF_2)_3$ by chemical analysis [Found: F, 31.7; Fe, 15.6; P, 25.7. $Fe(O_2PF_2)_3$ requires F, 31.8; Fe, 15.6; P, 25.9%], i.r. and Mössbauer spectroscopy, and *X*-ray powder photography. The powder photographs of the two new forms of $Fe(O_2PF_2)_3$ are sufficiently different to enable unambiguous characterisation to be carried out by this method.

The compound could also be obtained by the action of HPO_2F_2 upon β-$FeF_3{\cdot}3H_2O$. The reaction in diethyl ether can be represented by equation (3).

$$FeCl_3 + 3HPO_2F_2 \xrightarrow{Et_2O} Fe(O_2PF_2)_3 + 3HCl \quad (3)$$

An analogous reaction can be carried out using $AlCl_3$, which provides an alternative route to the previously reported[11]

Table 2. Infrared spectra (cm ¹) of difluorophosphates

		$Fe(O_2PF_2)_3$			
$Co(O_2PF_2)_2{\cdot}HPO_2F_2$	$Cr(O_2PF_2)_3{\cdot}HPO_2F_2$	*a*	*b*	$(HPO_2F_2)_n$[13]	Assignment
1 330s	1 345s	1 260s (sh)		1 335s,br	$\nu(P{=}O)$
1 280s	1 255vs	1 235s	1 245s		$\nu_{asym}(PO_2)$
1 140s	1 165vs	1 145s	1 165s		$\nu_{sym}(PO_2)$
1 060m	1 075m			1 070m	$\nu(P{-}OH)$
980s	960s	967s	967s	978s	$\nu_{asym}(PF_2)$
945s					
887s	910s,sp	906s	913m	888m	$\nu_{sym}(PF_2)$
555s	570w,br	590s	592w		$\delta(PO_2)$
520s (sh)					$\delta(PF_2)$
500s	495vs (sh)	500s	503m	490m	$\delta(POF) + \delta(PF_2)$
480s		492s			
365w		388m	385w,br		$\delta_{sym}(PF_2)$

[a] From the reaction of Fe with HPO_2F_2. [b] From the reaction of $FeCl_3$ in Et_2O with HPO_2F_2.

$Al(O_2PF_2)_3$ [Found: Al, 8.0; F, 34.4; P, 27.1. $Al(O_2PF_2)_3$ requires Al, 8.2; F, 34.6; P, 28.2%].

Results and Discussion

Halogenophosphoric acid solvates of the composition $M(O_2PX_2)_2\cdot2HPO_2X_2$ (X = Cl, M = Fe, Co, or Ni;[12] X = F, M = Zn[11]) have been reported previously. However, the formulations $M(O_2PF_2)_2\cdot HPO_2F_2$ and $M(O_2PF_2)_3\cdot HPO_2F_2$ are novel. The i.r. spectra of the $M(O_2PF_2)_2\cdot HPO_2F_2$ series, of which $Co(O_2PF_2)_2\cdot HPO_2F_2$ may be taken as typical (see Table 2), and $Cr(O_2PF_2)_3\cdot HPO_2F_2$ were similar. Essentially these spectra display a superposition of bands due to the acid and co-ordinated O_2PF_2 groups. No band assignable to the O–H stretch is observed, but all other HPO_2F_2 bands in the spectra of the solvates are virtually in the same positions as those for pure liquid HPO_2F_2.[13] Structural inferences concerning the HPO_2F_2 unit on the basis of vibrational spectra alone are however difficult because the vibrational frequencies of monomeric HPO_2F_2 are unknown (the pure acid is extensively hydrogen bonded in both the liquid and vapour phases[13]). Consideration of the PO_2 stretching frequencies due to the O_2PF_2 groups enables their likely mode of co-ordination to be deduced. The quantity $\Delta\nu = \nu_{asym}(PO_2) - \nu_{sym}(PO_2)$ enables bidentate to be distinguished from unidentate O_2PF_2.[6] For all the compounds reported here, $\Delta\nu$ lies in the range 70—142 cm^{-1} which is consistent with bidentate bridging co-ordination *via* oxygen, the most commonly observed bonding mode of the O_2PF_2 moiety.[5] Much higher $\Delta\nu$ values are observed when unidentate co-ordination takes place, *e.g.* 248 cm^{-1} for $SiMe_3(O_2PF_2)$.[14] A polymeric structure involving bridging difluorophosphate groups is also consistent with the observed involatility of these compounds and their insolubility in non-co-ordinating solvents (bidentate chelating O_2PF_2 is unknown and the reasons for this have been discussed [5]).

It is significant to note that since $Cr(O_2PF_2)_3\cdot HPO_2F_2$ probably contains three bidentate bridging O_2PF_2 groups per chromium, octahedral co-ordination can be achieved in this compound without any involvement of the HPO_2F_2 group. It is probable, in this solvate at least, that the HPO_2F_2 is not co-ordinated to the metal but is (presumably) hydrogen bonded to a PO_2F_2 group. This is in contrast to the previously reported dihalogenophosphoric acid solvates where co-ordination of the acid group *via* phosphoryl oxygen is proposed.[11,12]

The i.r. spectra of both new forms of $Fe(O_2PF_2)_3$ are similar (Table 2) and are consistent with the presence of only bidentate bridging O_2PF_2 groups.

Magnetic Properties.—The room-temperature magnetic moments ($\mu_{eff.}$) of the $M(O_2PF_2)_2\cdot HPO_2F_2$ series are displayed in Table 3. The moment of the manganese compound lies within the expected range for either an octahedral or tetrahedral high-spin d^5 system. For a high-spin d^6 system such as Fe^{II} the spin-only moment is 4.90 B.M.; a ground-state orbital contribution is expected for octahedral (ground ligand-field state $^5T_{2g}$) but not tetrahedral co-ordination (ground state ^5E). Thus for octahedral iron(II) compounds a magnetic moment of *ca.* 5.5 B.M. is expected,[15] whereas for tetrahedral co-ordination, moments in the range 4.9—5.1 B.M. are common. A high-spin octahedral cobalt(II) complex (d^7) has a $^4T_{1g}$ ground state and again a substantial orbital contribution to the spin-only value of 3.88 B.M. is expected; observed values are around 5.2 B.M.[15] For tetrahedral cobalt(II) complexes the ground-state term is $^4A_2$; no ground-state orbital contribution is expected but an excited-state orbital contribution results in observed moments in the range 4.4—4.8 B.M. For an octahedral nickel(II) complex (d^8) the ground state is $^3A_{2g}$ and no ground-state orbital contribution to the spin-only value of 2.83 B.M. is expected. Observed values for octahedral nickel(II) complexes usually lie between 2.9 and 3.3 B.M.[15] For a tetrahedral d^8 system the ground state is $^3T_1$ and a ground-state orbital contribution is expected; observed moments usually lie in the range 3.7—4.0 B.M. Thus the moments for the difluorophosphates of Fe^{II}, Co^{II}, and Ni^{II}, solvated by difluorophosphoric acid, are indicative of octahedral co-ordination of the metal. The moment of the nickel complex lies slightly outside the common range but there are several tetragonally distorted octahedral nickel complexes NiL_2X_2 (L = amine, X = halogen) which have moments between 3.3 and 3.5 B.M.[16] An approximately octahedral environment of the metal in the compounds $M(O_2PF_2)_2\cdot HPO_2F_2$ could be achieved either by (*a*) fluorine involvement in metal co-ordination, (*b*) the presence of tridentate oxygen [as observed in the compound $Cu(O_2PF_2)_2$ [17] where all the O_2PF_2 groups are essentially bridging bidentate but where some oxygens also make long contacts to copper], (*c*) the direct bonding of HPO_2F_2 to the metal, or (*d*) some combination of (*a*)—(*c*). The actual situation cannot be unambiguously deduced in the absence of single-crystal data. Attempts to prepare crystals of the $M(O_2PF_2)_2\cdot HPO_2F_2$ compounds have to date been unsuccessful.

Table 3. Magnetic data for $M(O_2PF_2)_2\cdot HPO_2F_2$ compounds

Metal	$\mu_{eff.}$/B.M.	T/K
Mn	5.95	293
Fe	5.53	293
Co	5.12	295
Ni	3.37	295

Mössbauer Spectra.—The Mössbauer data for $Fe(O_2PF_2)_2\cdot HPO_2F_2$ and both new forms of $Fe(O_2PF_2)_3$ are collected in Table 4. Data for the amorphous form of $Fe(O_2PF_2)_3$ [10] and $Fe(O_2PCl_2)_2\cdot2HPO_2Cl_2$ [11] are included for comparison. The $Fe(O_2PF_2)_2\cdot HPO_2F_2$ doublet could be further resolved into two pairs of doublets by least-squares methods. Each pair of resolved doublets has an isomer shift of 1.41 mm s^{-1} (quadrupole splittings 2.66 and 2.22 mm s^{-1}). These results indicate two crystallographically different iron sites and are consistent with a distorted octahedral environment for the iron atoms.[18] Integration of the areas of the resolved doublets indicates that the two iron sites are present in a 1:1 ratio.

The singlet for the form of $Fe(O_2PF_2)_3$ from the reaction of metallic iron and difluorophosphoric acid could be further resolved into two peaks (isomer shifts 0.43 and 0.66 mm s^{-1}, area ratio 3:2). Further resolution of the singlet for the form of $Fe(O_2PF_2)_3$ from the reaction of iron(III) chloride in ether with difluorophosphoric acid into two to four peaks was also

Table 4. Mössbauer data for iron halogenophosphates

Compound	Isomer shift	Quadrupole splitting	Linewidth (Γ) at half-height
		mm s^{-1}	
$Fe(O_2PF_2)_2\cdot HPO_2F_2$	$\left.\begin{array}{l}0.19\\2.63\end{array}\right\}1.41$	2.44	0.52 0.48
$Fe(O_2PCl_2)_2\cdot2HPO_2Cl_2$ [11]	1.49	2.81	
$Fe(O_2PF_2)_3$[a]	0.54		0.59
$Fe(O_2PF_2)_3$[b]	0.47		0.78
$Fe(O_2PF_2)_3$ [10]	0.64		0.35

[a] From the reaction of Fe with HPO_2F_2. [b] From the reaction of $FeCl_3$ in Et_2O with HPO_2F_2.

possible. However, none of the fits available was entirely satisfactory. The Mössbauer spectra of both forms of $Fe(O_2PF_2)_3$, reported here, are consistent with octahedral co-ordination of iron.[18] Octahedral co-ordination is to be anticipated for both forms since the i.r. spectra are consistent with the presence of three bidentate O_2PF_2 groups per iron atom.

Acknowledgements

We thank the S.E.R.C. for a Research Grant (including post-doctoral support to R. C. H.) and Dr. P. G. Harrison and Mr. N. W. Sharpe for their help in recording the Mössbauer spectra of the iron compounds.

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Received 22*nd June* 1984; *Paper* 4/1072