Crystal Structures of the Difluorophosphate Complexes, $Co(O_2PF_2)_2$·2MeCN and $Cu(O_2PF_2)_2$†

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The structures of two new difluorophosphates, $Co(O_2PF_2)_2$·2MeCN and $Cu(O_2PF_2)_2$, have been determined from single-crystal *X*-ray data. The former crystallises in the space group *Cmca*, $Z = 4$, with $a = 9.227(4)$, $b = 13.871(5)$, and $c = 9.471(4)$ Å, and the structure has been refined to $R = 0.046$ for 489 observed reflections. The compound is polymeric with bridging difluorophosphate groups, with the cobalt atom in octahedral co-ordination to four oxygen atoms and two nitrogen atoms from the *trans* oriented acetonitrile molecules. The copper compound belongs to the space group *Fddd*, $Z = 48$, with $a = 10.134(4)$, $b = 24.495(9)$, and $c = 34.058(10)$ Å, and the refinement converged at $R = 0.067$ for 1 587 observed reflections. It also has a polymeric structure with two independent copper atoms and bridging difluorophosphate groups. Each copper atom has four near oxygen neighbours but distorted-octahedral co-ordination is completed by two longer contacts to oxygen atoms of symmetry-related difluorophosphate groups. This tridentate function for the difluorophosphate group has not previously been observed.

Structural and bonding studies on compounds containing O_2PF_2 groups have mainly been carried out by means of vibrational and n.m.r. spectroscopy.[1] Some of us previously reported the preparation of a number of new transition-metal difluorophosphates[2] including the novel acid solvates $M(O_2PF_2)_2$·HPO_2F_2 (M = Mn, Fe, Co, or Ni). Although attempts to obtain crystals of these compounds were unsuccessful, we were able to isolate crystals of two previously unreported complexes, $Co(O_2PF_2)_2$·2MeCN and $Cu(O_2PF_2)_2$.

Table 1. Fractional co-ordinates for $Co(O_2PF_2)_2$·2MeCN

Atom	*X/a*	*Y/b*	*Z/c*
Co(1)	0.000 0	0.000 0	0.000 0
P(1)	0.250 0	0.038 2(2)	0.250 0
O(1)	0.156 7(5)	−0.012 8(3)	0.153 0(4)
F(1)	0.162 6(7)	0.112 1(5)	0.330 5(6)
N(1)	0.000 0	0.154 1(5)	0.025 9(8)
C(1)	0.000 0	0.228 5(7)	0.070 (1)
C(2)	0.000 0	0.324 9(8)	0.134 (1)

Experimental

Preparation of $Co(O_2PF_2)_2$·2MeCN.—Crystals of $Co(O_2PF_2)_2$·2MeCN were obtained by dissolving $Co(O_2PF_2)_2$·HPO_2F_2[2] in a minimum of HPO_2F_2 at 60 °C and then adding excess of MeCN. Upon standing for several weeks at room temperature, a small crop of red crystals was obtained. The compound could be more conveniently prepared (often in the form of a pale pink powder) by allowing MeCN to diffuse slowly into a concentrated solution of $Co(O_2PF_2)_2$·HPO_2F_2 in HPO_2F_2. The solid so precipitated was isolated by inert-atmosphere filtration and dried *in vacuo*. Prolonged drying *in vacuo* (10^{-4} Torr, *ca.* 1.33×10^{-2} Pa) caused loss of MeCN with a corresponding colour change from pink to blue.

The compound, which is very hygroscopic, was analysed conventionally for C, H, and N; phosphorus was determined by a wet oxidation method (Elemental Microanalysis Ltd.) and fluorine potentiometrically with a lanthanum fluoride ion-sensitive electrode (after heating in a sealed container with 10% sodium hydroxide at 120 °C for 24 h) [Found: C, 13.60; H, 1.80; F, 22.30; N, 7.95; P, 17.75. $Co(O_2PF_2)_2$·2MeCN requires C, 14.15; H, 2.10; F, 22.15; N, 8.25; P, 18.05%]. The i.r. spectrum of $Co(O_2PF_2)_2$·2MeCN in the range 4 000—350 cm^{-1} was recorded as a Nujol mull between silver chloride windows using a Perkin-Elmer 577 grating spectrometer.

Structure of $Co(O_2PF_2)_2$·2MeCN.—*Crystal data.* $C_4H_6CoF_4N_2O_4P_2$, $M = 342.9$, orthorhombic, $a = 9.227(4)$, $b = 13.871(5)$, $c = 9.471(4)$ Å, $U = 1\,212.2$ Å^3, $Z = 4$, $D_c = 1.88$ g cm^{-3}, $F(000) = 676$, space group *Cmca* from systematic absences and subsequent refinement, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 17.9$ cm^{-1}.

Structure determination. Data for 629 reflections, of which 489 were observed [$I > 3\sigma(I)$], were collected using a Hilger and Watts four-circle diffractometer using a crystal sealed in a thin-walled Lindemann tube and corrected for Lorentz and polarisation effects. The data reduction and subsequent calculations used the CRYSTALS program;[3] scattering factors, including anomalous dispersion contributions for all non-hydrogen atoms, were those for neutral atoms.[4] The structure was solved by Patterson and Fourier methods with the cobalt lying at the origin in a $2/m$ position. Following this, the phosphorus atom lies on a two-fold axis and the acetonitrile molecule on a mirror plane. The structure was refined by least-squares methods to $R = 0.113$ with isotropic and 0.046 with anisotropic thermal parameters. Refined atomic co-ordinates are listed in Table 1.

Preparation of $Cu(O_2PF_2)_2$.—Crystals of $Cu(O_2PF_2)_2$ were obtained as hygroscopic pale blue needles by allowing copper metal to react with anhydrous difluorophosphoric acid over a period of weeks. Dissolution of copper in HPO_2F_2 was slow and incomplete and crystals of $Cu(O_2PF_2)_2$ were removed from the mother-liquor and unreacted metal in a dry-box. The reaction of copper with difluorophosphoric acid was not a satisfactory method for the bulk preparation of $Cu(O_2PF_2)_2$, giving products with variable copper and phosphorus analyses. The identity of the compound was satisfactorily proved by *X*-ray crystallography.

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† *Supplementary data available* (No. SUP 56333, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 2. Fractional co-ordinates for $Cu(O_2PF_2)_2$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.5000	0.500 0	0.500 0	F(21)	0.770(2)	0.5976(5)	0.6611(3)
P(1)	0.7518(4)	0.478 3(2)	0.555 90(9)	F(22)	0.988(2)	0.5819(6)	0.6654(4)
O(11)	0.6505(9)	0.507 1(4)	0.534 6(2)	P(3)	0.6250	0.3274(2)	0.6250
O(12)	0.7072(9)	0.449 8(4)	0.592 4(2)	O(31)	0.7399(9)	0.3566(3)	0.6366(2)
F(11)	0.826(1)	0.439 3(6)	0.529 4(3)	F(31)	0.588(1)	0.2871(6)	0.6555(5)
F(12)	0.861(1)	0.518 5(6)	0.564 3(3)	O(41)	0.8157(8)	0.4210(3)	0.7018(2)
Cu(2)	0.7811(1)	0.434 81(6)	0.645 25(4)	P(4)	0.9108(5)	0.3825(3)	0.7202(1)
P(2)	0.8627(5)	0.553 6(1)	0.675 2(1)	F(41)	1.041(1)	0.4110(5)	0.7276(4)
O(21)	0.847(1)	0.549 0(4)	0.717 8(2)	F(42)	0.871(2)	0.3735(6)	0.7614(2)
O(22)	0.850(1)	0.506 7(4)	0.649 3(2)				

Table 3. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses for $Co(O_2PF_2)_2{\cdot}2MeCN$

Co(1)–O(1)	2.055(4)	O(1)–Co(1)–O(1)^a	90.5(3)
Co(1)–N(1)	2.152(7)	O(1)–Co(1)–N(1)	90.3(2)
P(1)–O(1)	1.444(4)	Co(1)–O(1)–P(1)	145.6(3)
P(1)–F(1)	1.511(5)	O(1)–P(1)–O(1)^b	121.3(4)
N(1)–C(1)	1.11(1)	O(1)–P(1)–F(1)	109.6(3)
C(1)–C(2)	1.47(1)	O(1)–P(1)–F(1)^b	109.3(3)
		F(1)–P(1)–F(1)^b	94.5(6)
		Co(1)–N(1)–C(1)	164.4(8)
		N(1)–C(1)–C(2)	177.8(11)

^{a} Symmetry operation $x, -y, -z$. ^{b} Symmetry operation $\frac{1}{2} + x, -y, \frac{1}{2} - z$.

Structure of $Cu(O_2PF_2)_2$.—*Crystal data.* $CuF_4O_4P_2$, M = 265.5, orthorhombic, a = 10.134(4), b = 24.495(9), c = 34.058(10) Å, U = 8 454.3 Å^3, Z = 48, D_c = 2.50 g cm^{-3}, $F(000)$ = 6 096, space group *Fddd* from systematic absences, Mo-K_α radiation, λ = 0.7107 Å, μ = 37.2 cm^{-1}.

Structure determination. Data were collected as described above for 2 074 reflections of which 1 587 with $I > 3\sigma(I)$ were considered observed. The asymmetric unit contains $1\frac{1}{2}$ formula units and possible positions for the two independent copper atoms were obtained using the MULTAN direct methods programs;[5] one copper lies on the inversion centre at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, the second is in a general position. Subsequent Fourier syntheses revealed the presence of two difluorophosphate groups, in general positions, a third [P(3)] lying on the two-fold axis at $\frac{5}{8},y,\frac{5}{8}$, and a fourth [P(4)] which is disordered about two positions close to the two-fold axis at $\frac{7}{8},\frac{3}{8},z$. The refinement converged at R = 0.152 with isotropic and 0.067 with anisotropic thermal parameters. During the refinement it was necessary to constrain the bond distances and angles in the disordered [P(4)] difluorophosphate group. Refined atomic co-ordinates are listed in Table 2.

Results and Discussion

Infrared Spectrum of $Co(O_2PF_2)_2{\cdot}2MeCN$.—The ν(C≡N) mode, as found for other acetonitrile adducts,[6] is shifted to higher energy and the value of $\Delta\nu$, *i.e.* $\nu_{asym}(PO_2) - \nu_{sym}(PO_2)$, at 125 cm^{-1} is consistent with the presence of bridging difluorophosphate groups as discussed previously.[2] The i.r. spectrum shows peaks at the following positions: 2 310m, 2 280m [ν(C≡N)], 1 280vs [$\nu_{asym}(PO_2)$], 1 155vs [$\nu_{sym}(PO_2)$], 1 038w [ρ(CH_2)], 935w [ν(C–C)], 895vs [$\nu_{asym}(PF_2)$], 855vs [$\nu_{sym}(PF_2)$], 555s [δ(PO_2)], and 495vs cm^{-1} [δ(POF)].

Structure of $Co(O_2PF_2)_2{\cdot}2MeCN$.—Bond distance and angle data are summarised in Table 3 and a diagram showing the unit-cell contents projected down the *a* axis is given in Figure 1. Because the cobalt lies on a special position, it is equidistant (2.055 Å) from four oxygen atoms with which it is coplanar. This distance can be compared with values of 2.080 and 2.111 Å in the related $Co[O_2P(OH)_2]_2{\cdot}2H_3PO_4$ complex[7] which contains bridging $O_2P(OH)_2$ groups. The fifth and sixth positions completing octahedral co-ordination are occupied at a distance of 2.152 Å by nitrogen atoms of the co-ordinated acetonitrile molecules. In the related $Cu_2Cl_4{\cdot}2MeCN$ and $Cu_3Cl_6{\cdot}2MeCN$ complexes,[6] the Cu–N distances are 1.96 and 1.97 Å respectively. There is little apparent distortion of the octahedron as, within the limits of the estimated standard deviations, the angles between *cis* atoms are 90°. As expected, the acetonitrile molecules are effectively linear, but the Co–N–C angle (164.4°) is significantly less than 180°. This is unusual and has previously been observed only with the copper complexes $CuCl_2{\cdot}1.5MeCN$ and $CuCl_2{\cdot}MeCN$.[6] In all other alkyl cyanide adducts the M–N–C angle is close to 180°.[6]

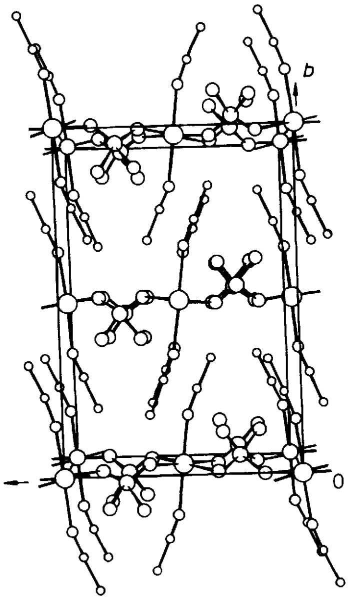

Figure 1. Projection of the unit-cell contents of $Co(O_2PF_2)_2{\cdot}2MeCN$ down the *a* axis

One consequence of the presence of bridging difluorophosphate groups is the formation in the overall structure of interlinked condensed 16-membered rings consisting of four cobalt and four difluorophosphate groups (see Figure 2). In related dihalogenophosphate structures[1] the repeating units are generally eight-membered rings based on two metal and two dihalogenophosphate groups although $AlMe_2(O_2PF_2)$ is believed to contain 12-membered rings.[8]

The P–O bond (1.444 Å) lies between those in the $O_2PF_2^-$ anion (KO_2PF_2, 1.470 Å)[9] and the bridging group in Ca(O$_2$-

Table 4. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses for $Cu(O_2PF_2)_2$

Cu(1)–O(11)	1.937(8)	O(11)–Cu(1)–O(21)	90.0(4)	O(12)–Cu(2)–O(12)[a]	76.1(4)
Cu(1)–O(21)[a]	1.900(9)	O(11)–Cu(1)–O(41)[a]	83.4(3)	O(12)–Cu(2)–O(31)[b]	108.2(3)
Cu(1)–O(41)[a]	2.622(5)	O(11)–Cu(1)–O(41)[b]	96.6(3)	O(22)–Cu(2)–O(31)	169.8(4)
P(1)–O(11)	1.440(9)	Cu(1)–O(11)–P(1)	145.4(6)	O(22)–Cu(2)–O(41)	91.3(3)
P(1)–O(12)	1.495(9)	O(11)–P(1)–O(12)	115.5(6)	O(22)–Cu(2)–O(12)[a]	101.9(4)
P(1)–F(11)	1.51(1)	O(11)–P(1)–F(11)	111.3(6)	O(22)–Cu(2)–O(31)[b]	164.9(3)
P(1)–F(12)	1.51(1)	O(11)–P(1)–F(12)	107.4(6)	O(31)–Cu(2)–O(41)	91.0(3)
P(2)–O(21)	1.466(9)	O(12)–P(1)–F(11)	110.6(7)	O(31)–Cu(2)–O(12)[a]	87.9(4)
P(2)–O(22)	1.453(9)	O(12)–P(1)–F(12)	111.6(5)	O(31)–Cu(2)–O(31)[b]	77.9(4)
P(2)–F(21)	1.51(1)	F(11)–P(1)–F(12)	99.3(9)	O(41)–Cu(2)–O(12)[a]	91.9(3)
P(2)–F(22)	1.48(1)	P(1)–O(12)–Cu(2)	136.6(6)	O(41)–Cu(2)–O(31)[b]	83.4(3)
Cu(2)–O(12)	1.984(8)	Cu(1)–O(21)–P(2)	132.5(6)	O(12)[a]–Cu(2)–O(31)[b]	164.9(3)
Cu(2)–O(22)	1.899(9)	O(21)–P(2)–O(22)	122.0(5)	Cu(2)–O(31)–P(3)	134.4(6)
Cu(2)–O(31)	1.982(8)	O(21)–P(2)–F(21)	107.6(7)	O(31)–P(3)–O(31)[a]	119.6(7)
Cu(2)–O(41)	1.988(6)	O(21)–P(2)–F(22)	110.6(7)	O(31)–P(3)–F(31)	110.2(6)
Cu(2)–O(12)[a]	2.479(9)	O(22)–P(2)–F(21)	108.4(7)	O(31)–P(3)–F(31)[a]	109.0(5)
Cu(2)–O(31)[c]	2.551(9)	O(22)–P(2)–F(22)	108.1(7)	F(31)–P(3)–F(31)[a]	96.3(16)
P(3)–O(31)	1.422(9)	F(21)–P(2)–F(22)	97.3(10)	Cu(2)–O(41)–P(4)	129.1
P(3)–F(31)	1.48(1)	P(2)–O(22)–Cu(2)	144.2(6)	O(41)–P(4)–O(41)[c]	119.4
P(4)–O(41)	1.49	O(12)–Cu(2)–O(22)	91.9(4)	O(41)–P(4)–F(41)	109.9
P(4)–O(41)[c]	1.472	O(12)–Cu(2)–O(31)	87.9(4)	O(41)–P(4)–F(42)	108.4
P(4)–F(41)	1.511	O(12)–Cu(2)–O(41)	167.9(4)	F(41)–P(4)–F(42)	98.7
P(4)–F(42)	1.477				

[a] Symmetry operation $\frac{5}{4} - x, y, \frac{5}{4} - z$. [b] Symmetry operation $x - \frac{3}{4}, 1 - y, z - \frac{3}{4}$. [c] Symmetry operation $\frac{5}{4} - x, \frac{3}{4} - y, z$.

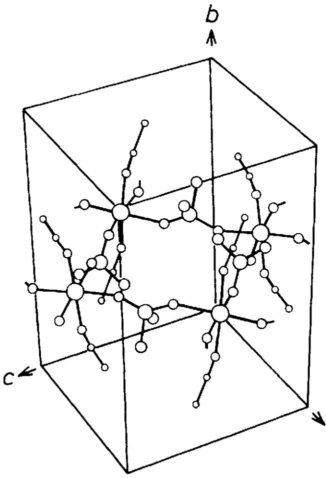

Figure 2. Orientation of the 16-membered rings in $Co(O_2PF_2)_2{\cdot}2MeCN$

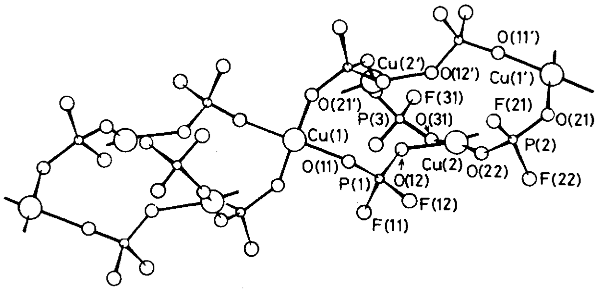

Figure 3. Repeating unit in $Cu(O_2PF_2)_2$ and atom numbering scheme (atoms carrying a prime are related to unprimed atoms by the symmetry operation $x,y,z \longrightarrow \frac{5}{4} - x,y,\frac{5}{4} - z$). The P(4) difluorophosphate group which interlinks these units has been omitted for clarity

$PF_2)_2{\cdot}2EtO_2CMe$ (1.41 Å).[10] The P–F distances observed here are also shorter (1.511 *vs.* 1.575 Å) than those in KO_2PF_2 but close to those in the adduct of the calcium salt (1.50 Å). The geometry at the phosphorus atom is distorted tetrahedral with the O–P–O and F–P–F angles (121.3 and 94.5°) showing the largest deviations. As expected, in the bridged structure the Co–O–P angles are all increased to 145.6°.

Structure of $Cu(O_2PF_2)_2$.—Bond distances and angles are collected in Table 4 and a diagram showing the repeating unit together with the atom numbering scheme is given in Figure 3.

This compound contains two independent copper atoms, Cu(1) lying on a centre of inversion (at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and Cu(2) in a general position. The unit cell thus contains 16 Cu(1) and 32 Cu(2) positions. There are also four independent bridging difluorophosphate groups which lead to a three-dimensional polymeric structure; the P(1) and P(2) groups are in general positions while P(3) lies on a two-fold axis (at $\frac{5}{8},y,\frac{5}{8}$) and the P(4) position is disordered about the two-fold axis at $\frac{7}{8},\frac{3}{8},z$.

Each of the two copper atoms is bonded to four oxygen atoms in a square-planar arrangement and distorted octahedral co-ordination is completed by two longer *trans* bonds to further oxygen atoms of symmetry-related difluorophosphate groups. The Cu(1) atoms are bonded to two sets of symmetry-related O(11) and O(21) atoms of, respectively, the P(1) and P(2) difluorophosphate groups at distances of 1.937 and 1.900 Å; by symmetry the O–Cu(1)–O bond angles are 90°. The longer contacts to two different symmetry-related O(41) atoms are 2.622 Å, comparable to the long oxygen distances observed in $Cu(PhCO_2)_2{\cdot}2H_2O$ (2.68 Å).[11]

The short Cu(2)–O bonds involve four different oxygen atoms, O(12), O(22), O(31), and O(41), with three of the distances averaging 1.985 Å while the fourth [to O(22)] is substantially shorter (1.899 Å). The bond angles at Cu(2) deviate from 90° with *trans* O–Cu(2)–O angles of 167.9 and 169.8°. The longer contacts, completing distorted-octahedral geometry, are to symmetry-related O(12) and O(31) atoms at 2.479 and 2.551 Å respectively; the distortion is shown by a variation in the *cis* O–Cu–O angles involving one of these longer contacts from 76.1 to 108.2° and a value of 164.9° for the *trans* O–Cu–O angle.

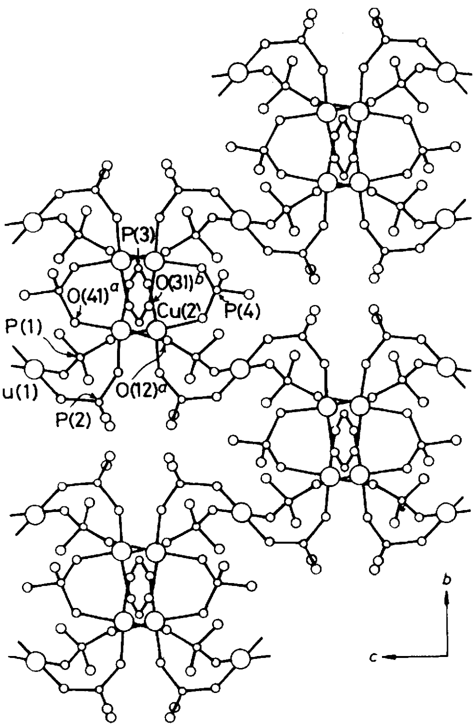

Figure 4. Projection of the unit-cell contents (0 to $c/2$) of $Cu(O_2PF_2)_2$ down the a axis. The fluorines at P(3) have been omitted for clarity

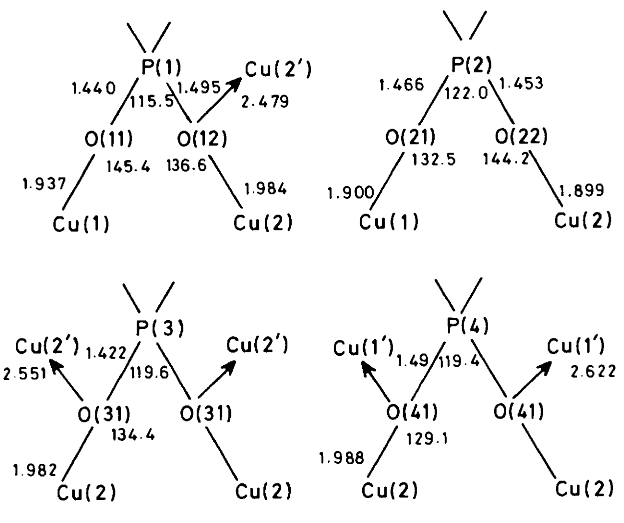

Figure 5. Bond distances (Å) and angles (°) for the four difluorophosphate groups in $Cu(O_2PF_2)_2$

As mentioned above, the four independent difluorophosphate groups bridge copper atoms, those based on P(1) and P(2) linking Cu(1) and Cu(2) while the P(3) and P(4) groups bridge pairs of Cu(2) atoms (see Figure 4). This leads to a three-dimensional structure containing 16-membered ring systems similar to those discussed above for the cobalt complex. In this case they comprise two Cu(1) and two Cu(2) atoms and two of each of the P(1) and P(2) difluorophosphate groups. The bridging groups thus generate infinite chains of such rings lying parallel to the c axis. The Cu(2) atoms in each ring are bridged by P(3) difluorophosphate groups and individual chains are interconnected by P(4) difluorophosphates.

The detailed environments of the four difluorophosphate groups are different and this is reflected in differences in the molecular parameters (see Figure 5) which cannot readily be rationalised. The P(3) and P(4) groups, which both involve two-fold axes, might be expected to be most similar. However, although the P–F distances and the O–P–O angles are very similar, the P–O distances and Cu–O–P angles are substantially different (the longer bond correlating with the smaller angle). Differences in the P–O bond lengths might then be expected to influence the Cu–O distances but these bonds differ by only 0.006 Å.

A possible reason for these differences is associated with the fact that both O(31) and O(41) are involved in longer contacts to Cu atoms, the former with Cu(2) and the latter with Cu(1). Only one of the oxygen atoms, O(12), of the P(1) difluorophosphate forms an extra interaction [with Cu(2)] and, although the P–O and 'shorter' Cu–O distances are comparable with those in the P(4) system, the P–O–P angle is substantially larger and the 'longer' Cu–O distance is shorter than the comparable P(4) parameters. Finally, in the P(2) group, which forms no longer Cu–O contacts, there are differences in the P–O lengths and the Cu–O–P angles, although the Cu–O distances are equal.

Perhaps the most unusual feature of this structure is the fact that three of the six oxygens of the difluorophosphate groups are effectively three-co-ordinate forming, in addition to a bond to phosphorus, one short (mean 1.96 Å) and one longer (mean 2.57 Å) bond to different copper atoms. These oxygen atoms are in effectively planar sp^2 hybridisation [the sums of the angles at O(12), O(31), and O(41) are 357.6, 359.7, and 356.7° respectively].

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Received 7th March 1985; Paper 5/393