Preparation and Crystal Structures of *trans*-$[Fe(NCMe)_2(Ph_2PCH_2PPh_2)_2][FeI_4]\cdot 2H_2O$ and $[Fe\{Ph_2P(O)CH_2P(O)Ph_2\}_3][I_3]_2$[†]

J. Elaine Barclay, David J. Evans, David L. Hughes and G. Jeffery Leigh*
AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, UK

In an attempt to characterise definitively the species previously reported to be $[Fe(NCMe)_2(dppm)]I_2$, the structure of $[Fe(NCMe)_2(dppm)_2][FeI_4]\cdot 2H_2O$ (dppm = $Ph_2PCH_2PPh_2$) has been determined. Thus dppm is capable of forming bis(bidentate) complexes with iron(II). However, such materials are air-sensitive, and in attempting to reproduce the synthesis of the dihydrate the novel diphosphine dioxide complex $[Fe(dppom)_3][I_3]_2$ [dppom = $Ph_2P(O)CH_2P(O)Ph_2$] was actually isolated and characterised by X-ray structure analysis. It is doubtful whether $[Fe(NCMe)_2(dppm)]I_2$ has ever been prepared.

We have recently described how the diphosphine $Ph_2PCH_2PPh_2$ (dppm) is apparently unable to form octahedral adducts $[FeX_2(dppm)_2]$ (X = halide) for steric reasons, but forms tetrahedral adducts such as $[FeI_2(dppm)_2]$ in which the diphosphine is monodentate.[1] It was also possible to isolate from acetonitrile an apparently six-co-ordinate adduct $[Fe(NCMe)_2(dppm)_2]I_2$, and a second species formulated as $[Fe(NCMe)_2(dppm)]I_2$, although Mössbauer spectroscopy indicated that both materials seemed to be *trans*-bis(acetonitrile)bis(diphosphine) complexes. We have now determined the structure of crystals thought to be of the second material and find that it is, in fact, *trans*-$[Fe(NCMe)_2(dppm)_2][FeI_4]\cdot 2H_2O$.

Results and Discussion

Crystal Structure of trans-$[Fe(NCMe)_2(dppm)_2][FeI_4]\cdot 2H_2O$.—The crystal comprises discrete $[Fe(NCMe)_2(dppm)_2]^{2+}$ cations and hydrogen-bonded chains of $[FeI_4]^{2-}$ anions with water molecules. Atomic coordinates are in Table 1 and selected molecular dimensions are in Table 2. The structures of the anion and cation are shown in Fig. 1.

In the cation the iron atom lies on a centre of symmetry and is co-ordinated in approximately octahedral fashion by the two diphosphine ligands, which form a rectangular equatorial plane, and the two acetonitrile ligands in *trans* form approximately normal to this plane. This is the first recording of a bis(dppm)-iron complex and the dimensions in the co-ordination sphere are much as expected for a low-spin iron(II) complex ion. The P–C–P plane is tilted at 28.1° from the equatorial FeP_4 plane, and there is considerable strain in the FeP_2C ring with angles of *ca.* 92° at the P atoms and 95.8(6)° at the C atoms. The Fe–P distances are accordingly slightly longer, mean 2.283(2) Å, than in similar iron complexes of $R_2PCH_2CH_2PR_2$, R = Et[2] or Me;[3] correspondingly, the Fe–N distance of 1.867(12) Å is marginally the shortest of its type reported.[2,4] The acetonitrile ligand is virtually linear, with normal N–C and C–C dimensions.

In two chelating mono(dppm)iron complexes, *viz.* the five-co-ordinate $[Fe(CO)_3(dppm)]$ molecule[5] and the piano-stool type complex ion $[Fe(C_5H_5)(CO)(dppm)]^+$,[6] the mean Fe–P distances are 2.217(8) and 2.212(14) Å, respectively.

The acute P–Fe–P angle [73.0(1)°] in our sample is coupled

Table 1 Final atomic coordinates (fractional × 10^4) for $[Fe(NCMe)_2(dppm)_2][FeI_4]\cdot 2H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Fe(1)	2500	2500	5000
P(1)	2330(2)	1324(3)	4131(2)
C(11a)	2468(7)	1629(8)	3256(8)
C(12a)	3060(7)	1889(10)	3301(8)
C(13a)	3190(7)	2188(11)	2692(9)
C(14a)	2713(10)	2230(11)	2010(10)
C(15a)	2121(8)	1965(11)	1940(8)
C(16a)	2011(7)	1640(10)	2577(8)
C(11b)	2636(7)	135(10)	4355(8)
C(12b)	2427(8)	−431(11)	4821(8)
C(13b)	2734(10)	−1303(10)	5085(8)
C(14b)	3233(8)	−1571(12)	4888(10)
C(15b)	3422(9)	−1000(13)	4436(11)
C(16b)	3120(8)	−165(12)	4154(9)
C(1)	1511(6)	1317(9)	3973(7)
P(2)	1474(2)	2537(3)	4318(2)
C(21a)	908(6)	2624(10)	4785(7)
C(22a)	640(7)	3509(12)	4831(8)
C(23a)	246(8)	3600(14)	5270(10)
C(24a)	130(8)	2839(15)	5659(10)
C(25a)	371(7)	1980(14)	5582(8)
C(26a)	766(6)	1881(11)	5156(8)
C(21b)	1184(7)	3313(11)	3486(9)
C(22b)	1366(7)	4274(13)	3616(9)
C(23b)	1135(8)	4942(13)	3040(12)
C(24b)	839(9)	4617(17)	2386(12)
C(25b)	673(8)	3651(19)	2245(10)
C(26b)	852(7)	3022(12)	2814(9)
N(3)	2298(5)	1645(8)	5637(6)
C(31)	2217(6)	1189(11)	6084(8)
C(32)	2092(10)	538(14)	6663(10)
Fe(2)	0	398(2)	7500
I(21)	322.1(5)	−723.2(8)	6564.5(6)
I(22)	−925.0(6)	1409.2(9)	6668.5(6)
O(5)	1136(6)	−672(9)	5207(6)

[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 2 Selected molecular dimensions (bond lengths in Å, angles in °) in $[Fe(NCMe)_2(dppm)_2][FeI_4]\cdot 2H_2O$ with e.s.d.s in parentheses

(*a*) About the cationic Fe atom			
Fe(1)–P(1)	2.281(4)	P(1)–Fe(1)–P(2)	73.0(1)
Fe(1)–P(2)	2.285(4)	P(1)–Fe(1)–N(3)	88.2(3)
Fe(1)–N(3)	1.867(12)	P(2)–Fe(1)–N(3)	87.3(3)
(*b*) In the nitrile ligands			
N(3)–C(31)	1.125(15)	Fe(1)–N(3)–C(31)	172.3(11)
C(31)–C(32)	1.525(22)	N(3)–C(31)–C(32)	177.4(15)
(*c*) In the anion			
Fe(2)–I(21)	2.651(2)	I(21)–Fe(2)–I(21′)	106.4(1)
Fe(2)–I(22)	2.617(2)	I(21)–Fe(2)–I(22)	106.0(1)
		I(21)–Fe(2)–I(22′)	112.3(1)
		I(22)–Fe(2)–I(22′)	113.7(1)
(*d*) In the hydrogen-bonded chains			
I(21) ··· O(5)	3.628(12)	Fe(2)–I(21) ··· O(5)	141.0(2)
I(22) ··· O(5″)	3.567(11)	Fe(2)–I(22) ··· O(5″)	104.9(2)
		I(21) ··· O(5) ··· I(22″)	139.4(4)

Primed numbers indicate atoms related by symmetry: ′ $-x, y, \frac{3}{2} - z$; ″ $-x, -y, 1 - z$; ‴ $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

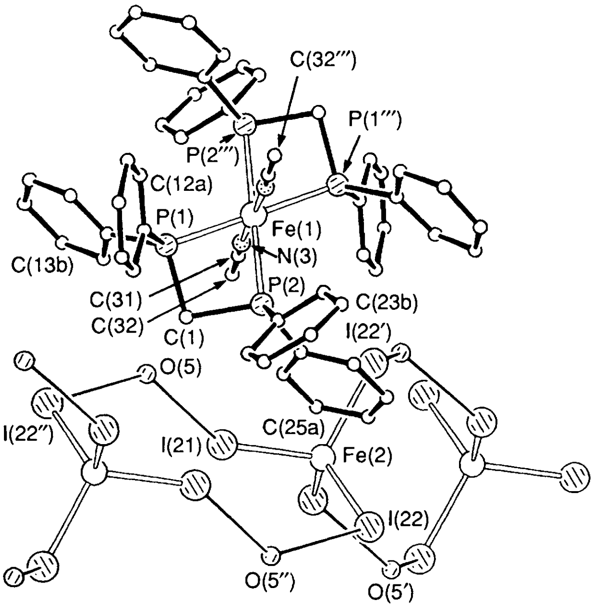

Fig. 1 View of a $[Fe(NCMe)_2(dppm)_2]^{2+}$ cation and part of the $[FeI_4]^{2-}/2H_2O$ hydrogen-bonded chain. The atomic numbering scheme is indicated; atoms in the phenyl rings are numbered as C(11a)–C(16a) *etc*. Symmetry relations denoted by primes are defined in Table 2

with the expected short P ··· P separation between phosphorus atoms of the same diphosphine ligand of 2.716(5) Å. The values obtained for the range of bis(diphosphine) complexes studied previously by us and others[2] are 3.01–3.36 Å, so that this represents by far the smallest bite angle reported in this series of compounds. This reinforces the idea that the CP_2Fe ring must be considerably strained, though there is no obvious reflection of unusual circumstances in the Mössbauer parameters.

The tetrahedral $[FeI_4]^{2-}$ anion lies on a two-fold symmetry axis with two quite different Fe–I bonds at 2.651(2) and 2.617(2) Å. Each iodide ligand is *ca*. 3.6 Å from an atom which we deduce must be the oxygen atom of a water molecule, and the difference in Fe–I bond lengths may be related to the strength of the hydrogen bonds which connect the anions and water molecules in long double-stranded chains parallel to the *c* axis. The hydrogen atoms of the water molecule have not been located, but dimensions in the hydrogen bonding (Table 2) suggest that at least one of the H atoms lies at some distance from an I ··· O vector.

Anions $[FeX_4]^{n-}$ (n = 1 or 2) are well known; there are many examples of structure determinations of crystals containing $[FeCl_4]^{n-}$ ions[7] and a few each for X = Br[8] or I.[9] The dimensions of our $[FeI_4]^{2-}$ ion are in accord with those in the literature, *e.g.* the Fe–I distances are similar to those in crystals of $[NEt_4]_2[FeI_4]$ and *ca*. 0.10 Å longer than those found in $[FeI_4]^-$ ions;[9] in the anions of $[Fe(HCHO)_6][FeI_4]_2\cdot I_2$ the four Fe–I distances show a wide range of values, 2.517(4)–2.567(4), mean 2.539(11) Å, although in that case there are some short iodide ligand contacts with the iodine molecule.[10] The difference in dimensions between the iron-(II) and -(III) ions is similar in several $[FeBr_4]^{n-}$ and $[FeCl_4]^{n-}$ examples.[7,8]

The crystals used for this X-ray structure determination were the red crystals isolated along with $[Fe(NCMe)_2(dppm)_2]I_2$, and we had previously characterised them as $[Fe(NCMe)_2(dppm)]I_2$,[1] based primarily upon analysis and a Mössbauer spectrum which was consistent with the presence of a single low-spin iron(II) site. The particular crystal used was initially very large, and we were forced to cut it down to a suitable size. We have now shown that the small crystals obtained at the same time, and which constituted the bulk of the material, are of the same structure as the large crystal since they yield identical Weissenberg photographs. Further, their Mössbauer spectrum consists of two doublets, isomer shift (i.s.) 0.19(1) and 1.06(1), quadrupole splitting (q.s.) 0.96(1) and 2.24(1), half-width 0.19(1) and 0.21(1) mm s^{-1}, respectively. Their analyses gave 44.2% C, 3.55% H and 2.65% N whereas $[Fe(NCMe)_2(dppm)_2][FeI_4]$ requires 43.9% C, 3.40% H, and 1.90% N. It will be noted that the calculated figures do not allow for the presence of $2H_2O$.

We prepared a further sample of $[Fe(NCMe)_2(dppm)_2]I_2$, as described earlier[1] [Found: C, 54.3; H, 4.30; N, 2.15%; i.s. 0.27(1), q.s. 0.75(1), half-width 0.25(1) mm s^{-1}. Required: C, 55.7; H, 4.35; N, 2.40%; lit.,[1] Mössbauer data are 0.26(1), 0.73(1), 0.18(1) mm s^{-1}] which appears to be authentic. It was allowed to react with 1 mole equivalent of FeI_2 to yield a powder containing 44.6% C, 3.55% H and 2.40% N and exhibiting a Mössbauer spectrum consisting of two doublets, i.s. 0.19(2) and 1.02(2), q.s. 0.87(2) and 2.08(2), and half-widths 0.14(2) and 0.21(2) mm s^{-1}. For further comparison, the Mössbauer parameters of FeI_2 and $[NBu^n_4]_2[FeI_4]$[11] are i.s. 1.12(1) and 0.96(1), q.s. 0.78(1) and 1.98(1), half-widths 0.19(1) and 0.35(1) mm s^{-1}. These data indicate fairly clearly that we have successfully synthesised $[Fe(NCMe)_2(dppm)_2][FeI_4]$. The Mössbauer data are not absolutely consistent, but it is known that quadrupole splittings are subject to solid-state effects,[12] and consideration of the following series shows that isomer shifts are not entirely independent of the matrix: $[Fe(NCMe)_2(depe)_2]X_2$ (depe = $Et_2PCH_2CH_2PEt_2$), i.s. 0.26(1) for X = $FeCl_4$, 0.28(2) for Br and 0.30(2) mm s^{-1} for I.[11]

It seems evident that adventitious water and/or air are implicated in the formation of crystalline $[Fe(NCMe)_2(dppm)_2][FeI_4]\cdot 2H_2O$. We were unable to resynthesise this material, and always obtained the anhydrous salt, as described above. A product which we did obtain, albeit in very low yield, in our attempt to reproduce the dihydrate, was shown by X-ray structure analysis to be $[Fe(dppom)_3][I_3]_2$ [dppom = $Ph_2P(O)CH_2P(O)Ph_2$]. A representation of the cation is in Fig. 2, atomic coordinates are in Table 3, and bond lengths and angles in Table 4.

The co-ordination about the iron is almost ideal octahedral, with angles very close to 90°. The Fe–O separations average 2.122(6) Å. The diphosphine dioxides are arranged in the expected propeller shape. The 'bite' of the diphosphine dioxide has a comfortable mean value of 3.006(15) Å, compared to 2.716(5) Å in the diphosphine itself. Although it should thus be a reasonable ligand for iron(II), there is no obvious precedent for this co-ordination. The only structurally characterised iron(II) diphosphine dioxide complex we could find is *cis*-$[FeCl_2$-

Table 3 Final atomic coordinates (fractional × 10^4) for $[Fe(dppom)_3][I_3]_2$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	5 178.3(7)	−2 315.4(8)	7 138.0(5)	C(3)	4 081(6)	−3 456(6)	5 968(4)
O(1)	6 741(3)	−2 341(4)	7 215(2)	O(4)	5 273(3)	−3 860(4)	7 186(2)
P(1)	7 630(2)	−2 834(2)	7 755(1)	P(4)	4 782(2)	−4 359(2)	6 724(1)
C(11a)	8 151(6)	−1 962(6)	8 122(4)	C(41a)	5 715(6)	−5 162(7)	6 552(4)
C(12a)	7 588(8)	−1 051(7)	8 003(5)	C(42a)	6 623(6)	−5 460(6)	6 965(4)
C(13a)	7 974(11)	−381(8)	8 286(6)	C(43a)	7 401(7)	−6 092(7)	6 894(5)
C(14a)	8 898(12)	−606(11)	8 676(7)	C(44a)^a	7 309(10)	−6 297(12)	6 315(8)
C(15a)	9 448(10)	−1 502(11)	8 799(7)	C(45a)^a	6 417(10)	−5 926(10)	5 845(6)
C(16a)	9 081(8)	−2 176(8)	8 524(5)	C(46a)^a	5 633(8)	−5 335(9)	5 950(6)
C(11b)	8 611(6)	−3 419(7)	7 494(4)	C(44x)^b	7 078(30)	−6 767(30)	6 631(20)
C(12b)	8 907(7)	−4 439(7)	7 667(5)	C(45x)^b	6 023(27)	−6 813(26)	6 347(17)
C(13b)	9 622(7)	−4 813(9)	7 406(5)	C(46x)^b	5 251(26)	−6 140(26)	6 429(17)
C(14b)	10 041(7)	−4 202(10)	6 968(6)	C(41b)	3 894(6)	−5 131(6)	7 014(5)
C(15b)	9 765(8)	−3 183(10)	6 783(6)	C(42b)	4 105(7)	−5 634(8)	7 677(5)
C(16b)	9 056(7)	−2 809(8)	7 058(5)	C(43b)	3 481(9)	−6 293(8)	7 928(6)
C(1)	7 275(5)	−3 812(5)	8 351(4)	C(44b)	2 678(9)	−6 462(9)	7 533(7)
O(2)	5 400(3)	−2 747(3)	8 153(2)	C(45b)	2 441(8)	−5 951(9)	6 884(7)
P(2)	6 223(1)	−3 454(1)	8 664.1(9)	C(46b)	3 061(7)	−5 287(8)	6 618(6)
C(21a)	6 672(6)	−2 895(5)	9 274(3)	O(5)	5 006(3)	−800(3)	7 100(2)
C(22a)	6 230(8)	−1 962(6)	9 231(5)	P(5)	4 177(2)	−185(2)	7 236(1)
C(23a)	6 509(9)	−1 511(7)	9 693(5)	C(51a)	3 298(6)	513(6)	6 500(5)
C(24a)	7 283(9)	−2 014(8)	10 211(5)	C(52a)	3 372(7)	326(7)	5 936(5)
C(25a)	7 744(7)	−2 950(8)	10 272(5)	C(53a)	2 640(9)	841(9)	5 391(6)
C(26a)	7 428(6)	−3 374(7)	9 806(4)	C(54a)	1 872(10)	1 484(10)	5 396(6)
C(21b)	5 809(6)	−4 601(6)	9 028(3)	C(55a)	1 776(9)	1 673(9)	5 949(7)
C(22b)	4 817(6)	−4 592(6)	9 061(4)	C(56a)	2 497(8)	1 204(8)	6 509(6)
C(23b)	4 455(7)	−5 448(8)	9 331(5)	C(51b)	4 664(7)	641(7)	7 657(6)
C(24b)	5 087(8)	−6 337(8)	9 577(4)	C(52b)	4 584(9)	611(8)	8 255(7)
C(25b)	6 089(8)	−6 364(7)	9 552(5)	C(53b)	5 061(12)	1 197(10)	8 603(10)
C(26b)	6 457(7)	−5 494(6)	9 293(4)	C(54b)	5 616(16)	1 844(16)	8 299(13)
O(3)	5 003(4)	−1 890(4)	6 128(2)	C(55b)	5 725(14)	1 906(14)	7 707(14)
P(3)	4 722(2)	−2 420(2)	5 648(1)	C(56b)	5 271(9)	1 303(9)	7 384(9)
C(31a)	5 785(6)	−2 907(8)	5 407(5)	C(5)	3 455(5)	−952(5)	7 721(3)
C(32a)	6 718(6)	−3 142(6)	5 822(4)	O(6)	3 585(3)	−2 284(3)	7 031(2)
C(33a)	7 543(8)	−3 601(9)	5 665(7)	P(6)	2 898(1)	−1 843(1)	7 361.2(9)
C(34a)^a	7 380(11)	−3 692(12)	5 033(9)	C(61a)	1 738(5)	−1 224(6)	6 816(4)
C(35a)^a	6 455(11)	−3 327(10)	4 565(7)	C(62a)	1 536(6)	−1 292(6)	6 204(4)
C(36a)^a	5 625(10)	−2 892(9)	4 730(6)	C(63a)	612(7)	−880(7)	5 795(4)
C(34x)^b	7 606(34)	−4 322(36)	5 474(25)	C(64a)	−99(7)	−429(7)	6 003(5)
C(35x)^b	6 709(28)	−4 350(27)	5 103(17)	C(65a)	80(7)	−343(7)	6 603(5)
C(36x)^b	5 717(26)	−3 875(26)	5 174(17)	C(66a)	987(6)	−754(7)	7 013(5)
C(31b)	3 901(6)	−1 634(7)	4 924(4)	C(61b)	2 514(5)	−2 750(5)	7 979(3)
C(32b)	2 975(6)	−1 844(7)	4 671(4)	C(62b)	2 340(6)	−3 653(6)	7 881(4)
C(33b)	2 412(8)	−1 205(8)	4 090(5)	C(63b)	1 945(7)	−4 338(7)	8 301(5)
C(34b)	2 746(8)	−375(9)	3 777(5)	C(64b)	1 720(7)	−4 133(8)	8 820(5)
C(35b)	3 655(9)	−168(11)	4 027(5)	C(65b)	1 899(7)	−3 251(9)	8 926(5)
C(36b)	4 240(8)	−795(10)	4 594(5)	C(66b)	2 302(7)	−2 542(7)	8 521(4)
In the I_3 anions							
I(71)	103.6(3)	2 105.3(7)	7 276.8(5)	I(82)	0	5 000	5 000
I(72)	1 477.7(5)	725.6(5)	8 390.1(4)	I(91)	1 252(2)	7 155(1)	1 095.3(9)
I(73)	2 898.5(9)	−677.0(6)	9 515.9(4)	I(92)	406.7(5)	5 680.0(7)	352.3(4)
I(81)	936.3(6)	6 685.8(6)	5 192.3(5)				

^{a} Site occupancy factor 0.75. ^{b} Site occupancy factor 0.25.

$(dppoe)_2][FeCl_4]$ [dppoe = $Ph_2P(O)CH_2CH_2P(O)Ph_2$], which has a mean bite of 2.831(14) Å, and Fe–O separations of 2.03(3) Å similar to ours;[13] the wider range of Fe–O distances here arises from the different opposed ligands in the *cis* complex.

Although our dioxide is not the major product of reaction, it is noteworthy that dppm is stable to air and moisture in the solid state and in solution. Evidently the iron helps to catalyse its oxidation.

We are left with the problem of $[Fe(NCMe)_2(dppm)]I_2$. The reported analysis[1] was not too different from that required for $[Fe(NCMe)_2(dppm)_2][FeI_4]$, but the Mössbauer spectrum showed no indication of the presence of $[FeI_4]^{2-}$. We can only assume that the sample obtained was actually very impure $[Fe(NCMe)_2(dppm)_2]I_2$. We have not been able to repeat its preparation, and its integrity and identity must be regarded with considerable suspicion.

We have shown that dppm can act as a bis(bidentate) ligand with iron(II). However, the products are not especially stable, and they are sensitive to moisture and/or dioxygen, particularly in solution. It is likely that a series of complexes could be isolated after exposing this system to controlled quantities of air and moisture, although we do not intend to pursue this.

Experimental

Most materials and techniques were as described earlier.[1] Mössbauer spectra were obtained using an E.S. Technology MS-105 spectrometer, recorded at 77 K and referenced against iron foil at 298 K.

trans-$[Fe(NCMe)_2(dppm)_2]I_2$.—Iron(II) iodide (0.41 g, 1.3 mmol) was treated with MeCN (*ca.* 20 cm^3) and the mixture

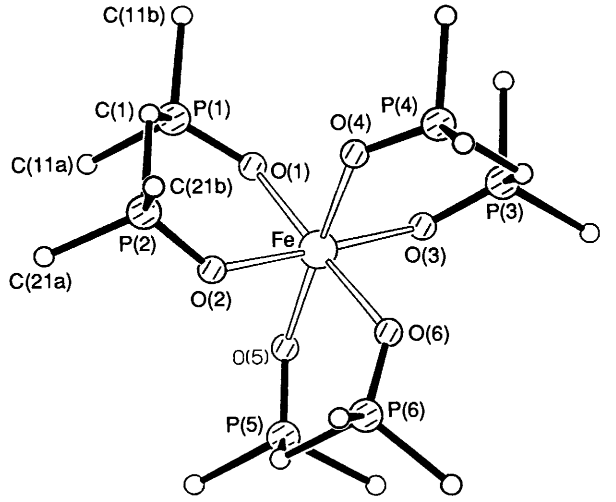

Fig. 2 View of the $[Fe(dppom)_3]^{2+}$ cation, with atomic numbering scheme. Only the α-C atoms of the phenyl rings are shown, for clarity

filtered. Then dppm (1.02 g, 2.6 mmol) was added and the mixture stirred for 1 h at 20 °C. The pink solid which precipitated was filtered off, washed with diethyl ether and dried at 10^{-3} mmHg (*ca.* 0.133 Pa). Yield 0.64 g, 42%.

trans-$[Fe(NCMe)_2(dppm)_2][FeI_4]\cdot 2H_2O$ *and* $[Fe(dppom)_3][I_3]_2$.—The complex $[Fe(NCMe)_2(dppm)_2]I_2$ (0.42 g, 0.36 mmol) was dissolved in MeCN (*ca.* 50 cm^3), FeI_2 (0.11 g, 0.36 mmol) was added and the solution stirred for about 2 h. It was then allowed to stand for 1 week. Deep red crystals formed which were filtered off and dried. The filtrate was stored at 0 °C for 1 week, when it produced a few deep red crystals. These were insufficient for analysis or for Mössbauer spectroscopy, and were subjected to X-ray structure analysis. They proved to be not the desired material, though they looked as if they were, but $[Fe(dppom)_3][I_3]_2$.

X-Ray Crystallographic Analyses.—*trans*-$[Fe(NCMe)_2(dppm)_2][FeI_4]\cdot 2H_2O$. *Crystal data.* $C_{54}H_{54}Fe_2I_4N_2O_2P_4$, $M = 1506.2$, monoclinic, space group $C2/c$ (no. 15), $a = 22.925(4)$, $b = 14.159(2)$, $c = 18.867(2)$ Å, $\beta = 108.96(1)°$, $U = 5791.8$ Å^3, $Z = 4$, $D_c = 1.727$ g cm^{-3}, $F(000) = 2928$, $\mu(\text{Mo-K}\alpha) = 27.6$ cm^{-1}, $\lambda(\text{Mo-K}\bar{\alpha}) = 0.710\,69$ Å.

Crystals were large, some more than 1 mm^3, and appeared to be coated in powdery microcrystals. Inside, they were clear, deep red and were chipped into rough fragments. One such piece, wedge-shaped, *ca.* 0.10 × 0.35 × 0.45 mm, was mounted on a glass fibre. After preliminary photographic examination, the crystal was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated Mo-Kα radiation) for determination of cell dimensions (from the centred settings of 25 reflections at $\theta = 10$–$11°$ in each of four diffracting orientations), and for measurement of diffraction intensities (to $\theta_{max} = 20°$). The data were corrected for Lorentz polarisation effects, slight deterioration (the intensities of two reflections dropped *ca.* 6.7% during data collection) and to eliminate negative intensities.

2679 Unique reflections were input to the SHELX program system[14] for structure determination (by automated Patterson methods in SHELXS[15]) and refinement (by full-matrix, least-squares methods), converging at $R = 0.066$ and $R' = 0.060$[14] for 2244 reflections (those with $I > \sigma_I$) weighted $w = (\sigma_F^2 + 0.000\,812F^2)^{-1}$. Hydrogen atoms in the dppm ligand were included in idealised positions, with parameters set to ride on those of their bonded C atoms. Coordinates of the H atoms of the acetonitrile ligands were taken from difference-map peaks; during refinement the C–H and H ··· H distances in this ligand were restrained towards normal values.

Table 4 Selected molecular dimensions (lengths in Å, angles in °) in $[Fe(dppom)_3][I_3]_2$ with e.s.d.s in parentheses

(*a*) About the Fe atom			
Fe–O(1)	2.109(5)	Fe–O(4)	2.139(5)
Fe–O(2)	2.121(5)	Fe–O(5)	2.104(5)
Fe–O(3)	2.118(5)	Fe–O(6)	2.143(5)
O(1)–Fe–O(2)	90.4(2)	O(3)–Fe–O(5)	89.9(2)
O(1)–Fe–O(3)	88.0(2)	O(4)–Fe–O(5)	176.9(2)
O(2)–Fe–O(3)	178.3(2)	O(1)–Fe–O(6)	178.4(2)
O(1)–Fe–O(4)	92.1(2)	O(2)–Fe–O(6)	91.2(2)
O(2)–Fe–O(4)	88.9(2)	O(3)–Fe–O(6)	90.4(2)
O(3)–Fe–O(4)	91.0(2)	O(4)–Fe–O(6)	87.7(2)
O(1)–Fe–O(5)	91.0(2)	O(5)–Fe–O(6)	89.3(2)
O(2)–Fe–O(5)	90.3(2)		
(*b*) In the ligands			
O(1)–P(1)	1.497(4)	O(2)–P(2)	1.499(4)
P(1)–C(11a)	1.780(10)	P(2)–C(21a)	1.789(9)
P(1)–C(11b)	1.789(9)	P(2)–C(21b)	1.782(8)
P(1)–C(1)	1.794(8)	C(1)–P(2)	1.810(9)
O(3)–P(3)	1.479(6)	O(4)–P(4)	1.491(6)
P(3)–C(31a)	1.791(11)	P(4)–C(41a)	1.802(10)
P(3)–C(31b)	1.785(7)	P(4)–C(41b)	1.788(9)
P(3)–C(3)	1.809(8)	C(3)–P(4)	1.830(7)
O(5)–P(5)	1.497(6)	O(6)–P(6)	1.494(6)
P(5)–C(51a)	1.802(8)	P(6)–C(61a)	1.789(6)
P(5)–C(51b)	1.783(12)	P(6)–C(61b)	1.789(7)
P(5)–C(5)	1.798(8)	C(5)–P(6)	1.811(8)
Fe–O(1)–P(1)	132.5(3)	Fe–O(2)–P(2)	130.5(3)
O(1)–P(1)–C(11a)	111.6(3)	O(2)–P(2)–C(21a)	110.2(3)
O(1)–P(1)–C(11b)	112.2(3)	O(2)–P(2)–C(21b)	111.9(3)
C(11a)–P(1)–C(11b)	107.5(4)	C(21a)–P(2)–C(21b)	108.8(4)
O(1)–P(1)–C(1)	110.3(3)	C(1)–P(2)–O(2)	112.5(3)
C(11a)–P(1)–C(1)	109.1(4)	C(1)–P(2)–C(21a)	108.5(4)
C(11b)–P(1)–C(1)	105.9(4)	C(1)–P(2)–C(21b)	104.8(4)
P(1)–C(1)–P(2)	115.9(4)		
Fe–O(3)–P(3)	132.6(3)	Fe–O(4)–P(4)	130.9(2)
O(3)–P(3)–C(31a)	112.9(4)	O(4)–P(4)–C(41a)	110.1(4)
O(3)–P(3)–C(31b)	112.7(4)	O(4)–P(4)–C(41b)	113.8(4)
C(31a)–P(3)–C(31b)	105.6(4)	C(41a)–P(4)–C(41b)	106.3(4)
O(3)–P(3)–C(3)	110.3(4)	C(3)–P(4)–O(4)	112.1(3)
C(31a)–P(3)–C(3)	107.7(5)	C(3)–P(4)–C(41a)	108.8(4)
C(31b)–P(3)–C(3)	107.3(4)	C(3)–P(4)–C(41b)	105.4(4)
P(3)–C(3)–P(4)	114.9(4)		
Fe–O(5)–P(5)	130.1(3)	Fe–O(6)–P(6)	129.1(3)
O(5)–P(5)–C(51a)	110.6(4)	O(6)–P(6)–C(61a)	111.2(4)
O(5)–P(5)–C(51b)	111.1(4)	O(6)–P(6)–C(61b)	113.8(3)
C(51a)–P(5)–C(51b)	110.2(4)	C(61a)–P(6)–C(16b)	103.6(3)
O(5)–P(5)–C(5)	111.8(3)	C(5)–P(6)–O(6)	112.3(3)
C(51a)–P(5)–C(5)	105.7(4)	C(5)–P(6)–C(61a)	108.2(3)
C(51b)–P(5)–C(5)	107.2(5)	C(5)–P(6)–C(61b)	107.2(4)
P(5)–C(5)–P(6)	113.2(4)		
(*c*) In the anions			
I(71)–I(72)	2.894(1)	I(71)–I(72)–I(73)	179.3(1)
I(72)–I(73)	2.949(1)		
I(81)–I(82)	2.885(1)	I(81)–I(82)–I(81′)	180.0
I(91)–I(92)	3.160(2)	I(91)–I(92)–I(92″)	179.3(1)
I(92)–I(92″)	2.956(2)		

Primes indicate symmetry-related positions: ′ $-x, 1-y, 1-z$; ″ $-x, 1-y, -z$.

A single, spherical, isolated peak, persistent in difference maps during the refinement, was later included as an oxygen atom. We assume this is of a water molecule which was present as an impurity, perhaps from the preparation of the dppm; the near neighbours (iodo ligands) of this atom are at reasonable hydrogen-bonding dimensions and support our identification of this atom. In a final difference map the highest peaks, *ca.* 0.7 e $Å^{-3}$, were close to either an iodo ligand or a dppm phenyl group.

For this determination and for that described below, scattering-factor curves for neutral atoms were taken from ref. 16. All computations, using programs noted above or listed in Table 4 of ref. 17, were performed on the MicroVAX II computer in this Laboratory.

$[Fe(dppom)_3][I_3]_2$. *Crystal data.* $C_{75}H_{66}FeI_6O_6P_6$, $M = 2066.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.684(1)$, $b = 14.082(1)$, $c = 22.253(1)$ Å, $\alpha = 73.698(6)$, $\beta = 100.950(5)$, $\gamma = 85.295(6)°$, $U = 3998.8$ $Å^3$, $Z = 2$, $D_c = 1.716$ g cm^{-3}, $F(000) = 1996$, μ(Mo-Kα) = 26.5 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

Crystals are deep red plates. Preliminary photographic examination indicated that some cell dimensions were similar to those of *trans*-$[Fe(NCMe)_2(dppm)_2][FeI_4]\cdot 2H_2O$, but from accurate centring of 25 reflections (θ = 10–11°), each in four orientations, on the CAD4 diffractometer, this sample was shown to be quite different.

Measurements on a crystal, *ca.* 0.21 × 0.21 × 0.24 mm, to $\theta_{max} = 22.5°$ yielded 10 418 unique reflections. These intensities were corrected for Lorentz polarisation effects, absorption (by semiempirical ψ-scan methods) and to eliminate negative intensities (by Bayesian statistical methods); no deterioration correction was necessary.

In the SHELX system, the structure was determined from direct methods (to locate six iodine atoms and the iron atom) and subsequent electron-density maps. There are three independent I_3^- ions in the structure: one is in a general position, one lies on a centre of symmetry (the central I on the inversion centre), and the third is disordered about a centre of symmetry (the centre is close to the midpoint of an I–I bond). In the cation a pair of neighbouring parallel phenyl rings have corresponding alternative orientations, with a site-occupancy ratio of *ca.* 3:1. Refinement was by large-block-matrix least-squares methods. All the non-hydrogen atoms (except for the C atoms in the minor sites of the disordered phenyl rings) were refined anisotropically, and hydrogen atoms were included in idealised positions with free isotropic thermal parameters. At convergence, $R = 0.069$ and $R' = 0.061$ for 8587 reflections (those with $I > \sigma_I$) weighted $w = (\sigma_F^2 + 0.000\,304F^2)^{-1}$. The only significant peaks in a final difference map, at *ca.* 1.2 e $Å^{-3}$, were close to the disordered I_3^- ion.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

References

1 J. E. Barclay, G. J. Leigh, A. Houlton and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1988, 2865.

2 J. E. Barclay, A. Hills, D. L. Hughes and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1988, 2871.

3 M. Di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1981, **20**, 3430.

4 See, for example, V. L. Goedken, Y. Park, S.-M. Peng and J. M. Norris, *J. Am. Chem. Soc.*, 1974, **96**, 7693; H. W. Smith, B. D. Santarsiero and E. C. Lingafelter, *Cryst. Struct. Commun.*, 1979, **8**, 49.

5 F. A. Cotton, K. I. Hardcastle and G. A. Rusholme, *J. Coord. Chem.*, 1973, **2**, 217.

6 R. B. English and M. M. de V. Steyn, *Acta Crystallogr., Sect. B*, 1979, **35**, 954.

7 See, for example, G. Schmidt, G. Barbenheim and R. Boese, *Z. Naturforsch., Teil B*, 1985, **40**, 787; I. P. Lavrentiev, L. G. Korableva, E. A. Lavrentieva, G. A. Nifontova, M. L. Khidekel, I. G. Gusakovskaya, T. I. Larkina, L. D. Arutyunian, O. S. Filipenko, V. I. Ponomarev and L. O. Atovmyan, *Transition Met. Chem.*, 1980, **5**, 193; D. J. Evans, A. Hills, D. L. Hughes and G. J. Leigh, *Acta Crystallogr., Sect. C*, 1990, **46**, 1818.

8 See, for example, G. D. Sproul and G. D. Stucky, *Inorg. Chem.*, 1972, **11**, 1647; U. Russo, G. Valle, G. J. Long and E. O. Schlemper, *Inorg. Chem.*, 1987, **26**, 665.

9 W. Saak and S. Pohl, *Z. Kristallogr.*, 1986, **174**, 173; S. Pohl and W. Saak, *Z. Anorg. Allg. Chem.*, 1985, **523**, 25.

10 W. Saak and S. Pohl, *Z. Anorg. Allg. Chem.*, 1987, **552**, 186.

11 J. E. Barclay, D. J. Evans, G. J. Leigh, J. Silver and L. Slade, unpublished work.

12 D. J. Evans, A. Hills, D. L. Hughes, G. J. Leigh, A. Houlton and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1990, 2735.

13 D. C. Povey, T. S. Lobana and P. K. Bhatia, *J. Cryst. Spectrosc. Res.*, 1991, **21**, 13.

14 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.

15 G. M. Sheldrick, *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Clarendon Press, Oxford, 1985, pp. 175–189.

16 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

17 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

Received 2nd July 1992; *Paper* 2/03502B