New Binuclear Iron–Vanadium Complexes of Arylazo Oximates. Crystal Structure of $[Fe(PhN{=}NCPh{=}NO)_3VO(bipy)]PF_6$ (bipy = 2,2′-bipyridine)†

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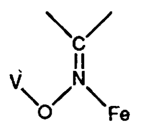
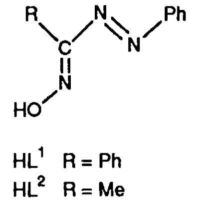
Binuclear iron(II)–vanadium(IV) complexes of types $[FeL_3VO(acac)]$ **1** and $[FeL_3VO(diam)]PF_6$ **2** have been prepared where HL is PhN=NC(R)=NOH with R = Ph(HL^1) or Me(HL^2), Hacac is acetylacetone and diam is 2,2′-bipyridine (bipy), 1,10-phenanthroline or 3,5-dimethyl-1-(2-pyridyl)pyrazole. Complexes of type **1** are obtained from $Na[FeL_3]\cdot H_2O$ and $[VO(acac)_2]$ and **2** by adding diam to acidified **1**. The crystal structure of $[FeL^1_3VO(bipy)]PF_6$ has been determined. The low-spin iron(II) atom is facially tris chelated in the $Fe(N,N)_3$ fashion and the three pendant oximato oxygen atoms engage the vanadium atom which is also bonded to an oxo oxygen and bipy nitrogen atoms. The VO_4N_2 co-ordination sphere is distorted octahedral. The *trans* influence of the oxo oxygen lengthens a V–O(oximate) bond by 0.2 Å. The complexes behave as one-electron paramagnets due to the VO^{2+} centre. Their ESR spectra are axial with $g_{\parallel} < g_{\perp}$. The ^{51}V hyperfine interaction follows the trend **1** > **2**.

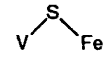
Current interest in the chemistry of discrete tetra- and pentavalent vanadium complexes in the environment of N- and/or O-donor ligands[1–9] has originated to a large extent from the proven or probable existence of such species in the living world as in amavadin, algal bromoperoxidase, ascidium blood and vanadium-treated biomolecules.[10–15] In this work we describe a novel heterobinuclear family of VFe complexes in which the metal atoms are O,N bridged, **I**, by the oxime function of arylazo oximes, **II** (R = Ph or Me). Molecular VFe complexes are rare and the few authentic examples known mostly have the sulphide bridge **III** and nuclearity >2.[16–18]



I



II



III

Results and Discussion

Synthesis and Characterisation.—The two arylazo oximes HL^1 and HL^2 of type **II** will be generally abbreviated as HL. The eight complexes reported in this work (Table 1) belong to two types: $[FeL_3VO(acac)]$ **1** and $[FeL_3VO(diam)]PF_6$ **2**. Here $acac^-$ is the acetylacetonate ion and diam is a diamine like 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) or 3,5-dimethyl-1-(2-pyridyl)pyrazole (dmppz).

$$Na[FeL_3] + [VO(acac)_2] \longrightarrow \underset{\mathbf{1}}{[FeL_3VO(acac)]} + Na(acac) \quad (1)$$

$$\mathbf{1} + H^+ + diam + PF_6^- \longrightarrow \underset{\mathbf{2}}{[FeL_3VO(diam)]PF_6} + Hacac \quad (2)$$

Reactions (1) and (2) were used for preparing the complexes. Both are very facile, *e.g* the formation of **1** occurs simply upon mixing $[VO(acac)_2]$ and $Na[FeL_3]\cdot H_2O$[19,20] in dichloromethane. Here the structural unit **I** is assembled *via* displacement of a bound acac ligand by oximato oxygen atoms of the L^- ligands which are already tris chelated to an iron(II) atom in N,N fashion (see structure below). In the synthesis of **2**, equation (2), a solution of **1** in acidified methanol is treated with an equimolar amount of diam (and excess of NH_4PF_6). The binuclear moiety of **1** is retained; only $acac^-$ is displaced by diam with assistance from protons.

Selected characterisation data are collected in Table 1. The solids are dark coloured and solutions in polar organic solvents are blue-green. Complexes **1** and **2** are respectively non-electrolytes and 1:1 electrolytes in acetonitrile solution. All species have one unpaired electron corresponding to the presence of VO^{2+} ($S = \frac{1}{2}$) in combination with low-spin iron(II) ($S = 0$). The V=O stretch lies in the range 960–975 cm^{-1}. Intense electronic transitions observed at 600 and 400 nm are characteristic[19,20] of the $[FeL_3]^-$ moiety and vitiate observation of the vanadium ligand-field transitions.

Structure of $[FeL^1{}_3VO(bipy)]PF_6$.—The complexes reported in this work generally failed to afford X-ray-quality crystals. The above bipy complex is an exception but even here diffraction was relatively weak. A satisfactory structure could, however, be derived from the data revealing all essential features of bonding. A view of the binuclear cation (with the six phenyl rings omitted for clarity) is shown in Fig. 1 in which the vanadium co-ordination sphere is displayed as an inset. Selected bond distances and angles are given in Table 2.

The three arylazo oximate ligands tris chelate the iron(II) atom in the facial mode utilising azo and oxime nitrogen atoms. The three pendant oximato oxygen atoms occupy a triad of facial sites around vanadium(IV) which is additionally bonded to the two bipy nitrogen atoms and an oxo oxygen atom. The two metal atoms thus have three oximato bridges of type **I** between them. The V ··· Fe distance is 3.590(1) Å.

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† 2,2′-Bipyridine-1κ^2*N*,*N*′oxo-1κ*O*-tris(μ-α-phenylazo-2κ*N*^{2}-benzaldehyde oximato-2κ*N*,1κ*O*)iron(II)vanadium(IV) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-S.I. unit employed: G = 10^{-4} T.

Table 1 Characterisation data

Compound	Elemental analysis (%)[a] C	H	N	μ_{eff}[b]	Λ_M[c]/Ω cm² mol⁻¹	ν(V=O)[d]/cm⁻¹	UV/VIS[c] λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹)
$[FeL^1_3VO(acac)]$	58.80 (59.0)	4.10 (4.15)	13.80 (14.10)	1.60	*e*	960	605 (7100), 400 (14 450), 270 (53 400)
$[FeL^1_3VO(bipy)]PF_6$	53.85 (53.65)	3.70 (3.45)	13.95 (14.05)	1.78	128	965	580 (9000), 380 (15 400), 260 (60 800)
$[FeL^1_3VO(phen)]PF_6$	54.80 (54.65)	3.50 (3.40)	13.85 (13.75)	1.74	142	965	580 (9850), 380 (16 800), 260 (79 200)
$[FeL^1_3VO(dmppz)]PF_6$	52.50 (52.70)	3.80 (3.70)	15.15 (15.10)	1.65	116	970	580 (8450), 385 (14 850), 255 (59 350)
$[FeL^2_3VO(acac)]$	49.10 (49.15)	4.20 (4.40)	17.70 (17.80)	1.65	*e*	970	595 (5100), 380 (15 700), 260[f] (24 650)
$[FeL^2_3VO(bipy)]PF_6$	44.80 (44.85)	3.50 (3.50)	16.60 (16.95)	1.82	136	970	570 (6330), 370 (18 500), 275[f] (25 100)
$[FeL^2_3VO(phen)]PF_6$	46.15 (46.25)	3.55 (3.45)	16.55 (16.50)	1.74	137	975	570 (6300), 370 (19 200), 270 (44 200)
$[FeL^2_3VO(dmppz)]PF_6$	43.80 (44.05)	4.00 (3.80)	18.05 (18.15)	1.79	114	975	570 (5800), 375 (18 500), 275[f] (26 200)

[a] Calculated values are in parentheses. [b] At 298 K. [c] In acetonitrile. [d] In KBr disk. [e] Non-electrolyte. [f] Shoulder.

Table 2 Selected bond lengths (Å) and angles (°) for $[FeL^1_3VO(bipy)]PF_6$

Fe–N(3)	1.942(11)	Fe–N(5)	1.906(11)
Fe–N(6)	1.940(10)	Fe–N(8)	1.925(11)
Fe–N(9)	1.958(10)	Fe–N(11)	1.906(11)
V–O(1)	1.608(9)	V–O(2)	2.041(9)
V–O(3)	2.002(9)	V–O(4)	2.256(9)
V–N(1)	2.105(11)	V–N(2)	2.121(12)
N(3)–Fe–N(5)	78.5(4)	N(3)–Fe–N(6)	97.7(4)
N(3)–Fe–N(8)	168.0(4)	N(3)–Fe–N(9)	98.9(4)
N(3)–Fe–N(11)	99.1(4)	N(5)–Fe–N(6)	99.0(4)
N(5)–Fe–N(8)	91.0(4)	N(5)–Fe–N(9)	167.0(4)
N(5)–Fe–N(11)	89.6(4)	N(6)–Fe–N(8)	78.0(5)
N(6)–Fe–N(9)	94.0(5)	N(6)–Fe–N(11)	162.4(4)
N(8)–Fe–N(9)	92.6(4)	N(8)–Fe–N(11)	86.6(5)
N(9)–Fe–N(11)	78.1(5)	O(1)–V–O(2)	98.4(4)
O(1)–V–O(3)	99.2(4)	O(1)–V–O(4)	176.5(4)
O(1)–V–N(1)	98.7(5)	O(1)–V–N(2)	98.2(5)
O(2)–V–O(3)	95.3(4)	O(2)–V–O(4)	82.8(3)
O(2)–V–N(1)	160.5(4)	O(2)–V–N(2)	92.2(4)
O(3)–V–O(4)	83.9(3)	O(3)–V–N(1)	90.9(4)
O(3)–V–N(2)	159.8(4)	O(4)–V–N(1)	79.5(4)
O(4)–V–N(2)	78.4(4)	N(1)–V–N(2)	76.4(4)

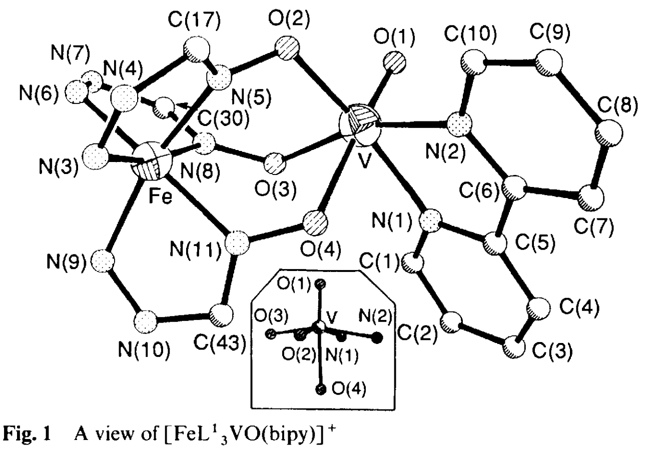

Fig. 1 A view of $[FeL^1_3VO(bipy)]^+$

In the VO_4N_2 co-ordination sphere the metal atom is displaced by 0.31 Å from the near perfect plane formed by O(2), O(3), N(1) and N(2) towards the oxo oxygen, O(1) (inset in Fig. 1). The average V–N distance is 2.113(12) Å which compares well with those[5] in other bipy complexes of VO^{2+}. The V–O distances are of three distinct types: 1.608(9), V–O(1); 2.021(9), average of V–O(2) and V–O(3); and 2.256(9) Å, V–O(4). Taking 2.021(9) Å as the normal V–O(oximate) length, the *trans* influence of oxo oxygen on the V–O(4) bond amounts to a lengthening of 0.2 Å. To our knowledge no other oximate-*O* complex of V exists. The bipy ligand is planar (mean deviation 0.025 Å) but the vanadium atom is situated 0.17 Å above the plane.

The FeN_6 co-ordination sphere is distorted octahedral with average Fe–N distances of 1.947(11) (azo) and 1.912(11) Å (oxime). The chelate rings are good planes. Interestingly, the surface areas of the triangles defined by three N(azo), three N(oxime) and three O(oxime) atoms are 3.69, 3.10 and 3.61 Å² respectively. Thus the molecule is shaped such that there is a slight constriction at the N(oxime) face compared to the N(azo) and O(oxime) faces. The distances and angles within the chelate rings are comparable to those in other structurally characterised arylazo oximates.[21]

The ability of the $[FeL_3]^-$ moiety to act as an efficient facial O_3 ligand has been noted earlier in our works on trinuclear species of type $[M(FeL_3)_2]^{z+}$ (M^{II}, $z = 0$; M^{III}, $z = 1$) in which the two $[FeL_3]^-$ units together create a pseudo-octahedral co-ordination sphere around the central M atom.[20,22,23] Similar trinucleation based on oximato bridging has also been observed in related systems.[21,24,25] The $[FeL^1_3VO(bipy)]PF_6$ complex and by inference **1** and **2** in general represent a novel oximato-bridged binuclear type.

ESR Spectra.—In frozen (77 K) acetonitrile–toluene (1:1) glass the complexes given rise to well resolved ESR spectra having ^{51}V ($I = \frac{7}{2}$) hyperfine structure. No nitrogen super-hyperfine structure is observed for any of the complexes. Spectra for two representative complexes are shown in Fig. 2, and spectral parameters for the whole family are listed in Table 3. The spectra have axial symmetry with $g_{\parallel} < g_{\perp}$. The unpaired electron is in the d_{xy} orbital (axial compression) as expected for VO^{2+} complexes.[26] An interesting trend relates to the ^{51}V hyperfine interaction which systematically follows the order **1** > **2**, *i.e.* $VO_6 > VO_4N_2$ (Fig. 2, Table 3). The higher nucleophilicity of the diam nitrogen compared to the acac⁻ oxygen is a plausible reason for this trend.[26]

Conclusion

The ability of facial $[FeL_3]^-$ to sequester metal ions *via* the oximato oxygen triad has been successfully applied to vanadium(IV) and in this manner the first examples of binuclear

O,N-bridged FeV complexes have been realised in the form of [FeL$_3$VO(acac)] and [FeL$_3$VO(diam)]PF$_6$. Structure determination has revealed that the metal atoms have three bridges of type **I** between them in the case of [FeL$^1{}_3$VO(bipy)]PF$_6$ and by inference in all the eight complexes reported. The iron(II) co-ordination sphere is uniformly FeN$_6$ (low spin) while that of vanadium(IV) ($S = \frac{1}{2}$) is either VO$_6$ (acac complexes) or VO$_4$N$_2$ (diam complexes). The ESR ^{51}V hyperfine coupling constants follow the order VO$_6$ > VO$_4$N$_2$ corresponding to the nucleophilicity order diam > acac$^-$.

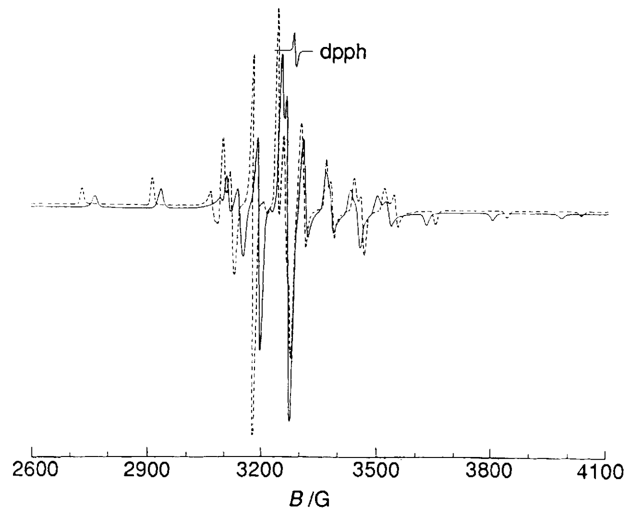

Fig. 2 X-Band ESR spectra of [FeL$^1{}_3$VO(bipy)]PF$_6$ (——) and [FeL$^1{}_3$VO(acac)] (- - -) in acetonitrile–toluene (1:1) glass (77 K); dpph = diphenylpicrylhydrazyl

Experimental

Materials.—Arylazo oximes,[27] Na[FeL$_3$]·H$_2$O,[19,20] [VO(acac)$_2$],[28] and dmppz[29] were prepared by reported methods. All other salts, ligands, chemicals and solvents were of analytical grade available commercially.

Measurements.—Physical measurements were made as follows: UV/VIS/NIR spectra, Hitachi 330 spectrophotometer;

Table 3 Frozen-solution (77 K) ESR data*

Compound	$g_{\parallel}(A_{\parallel}/G)$	$g_{\perp}(A_{\perp}/G)$
[FeL$^1{}_3$VO(acac)]	1.944(187)	1.992(70)
[FeL$^1{}_3$VO(bipy)]PF$_6$	1.949(174)	1.986(64)
[FeL$^1{}_3$VO(phen)]PF$_6$	1.944(179)	1.985(65)
[FeL$^1{}_3$VO(dmppz)]PF$_6$	1.950(174)	1.988(64)
[FeL$^2{}_3$VO(acac)]	1.942(187)	1.993(70)
[FeL$^2{}_3$VO(bipy)]PF$_6$	1.950(177)	1.995(64)
[FeL$^2{}_3$VO(phen)]PF$_6$	1.947(179)	1.995(65)
[FeL$^2{}_3$VO(dmppz)]PF$_6$	1.950(173)	1.994(65)

* In acetonitrile–toluene (1:1).

Table 4 Atomic coordinates* ($\times 10^4$) for [FeL$^1{}_3$VO(bipy)]PF$_6$

Atom	*x*	*y*	*z*
Fe	6 915(1)	5 016(1)	1 549(1)
V	8 290(1)	4 936(2)	490(1)
O(1)	8 158(6)	4 552(6)	−231(4)
O(2)	7 203(5)	5 602(5)	344(4)
O(3)	7 896(6)	3 945(5)	921(4)
O(4)	8 538(5)	5 526(5)	1 488(4)
N(1)	9 538(7)	4 576(7)	874(5)
N(2)	8 970(7)	6 038(7)	370(5)
N(3)	6 543(6)	6 065(7)	1 865(5)
N(4)	6 431(7)	6 709(6)	1 490(5)
N(5)	6 897(6)	5 767(6)	842(5)
N(6)	5 830(6)	4 495(7)	1 226(5)
N(7)	5 794(7)	3 748(7)	959(5)
N(8)	7 169(7)	4 069(6)	1 059(5)
N(9)	7 175(7)	4 370(6)	2 362(5)
N(10)	7 939(7)	4 287(6)	2 660(5)
N(11)	8 087(6)	5 177(6)	1 850(5)
C(1)	9 778(10)	3 823(11)	1 143(8)
C(2)	10 578(10)	3 640(9)	1 454(7)
C(3)	11 164(10)	4 268(11)	1 499(8)
C(4)	10 940(9)	5 048(11)	1 238(7)
C(5)	10 120(9)	5 208(9)	925(6)
C(6)	9 798(10)	5 984(9)	619(6)
C(7)	10 304(10)	6 717(10)	594(7)
C(8)	9 917(12)	7 420(12)	279(8)
C(9)	9 095(11)	7 459(11)	26(8)
C(10)	8 629(11)	6 754(12)	77(8)
C(11)	6 356(9)	6 209(8)	2 481(6)
C(12)	5 572(10)	6 468(9)	2 498(7)
C(13)	5 413(13)	6 540(12)	3 132(10)
C(14)	6 032(13)	6 423(11)	3 661(9)
C(15)	6 785(10)	6 193(10)	3 639(7)
C(16)	6 959(9)	6 080(9)	3 035(7)
C(17)	6 612(8)	6 542(9)	896(7)
C(18)	6 553(9)	7 244(9)	422(7)
C(19)	6 389(9)	7 129(9)	−210(7)
C(20)	6 330(10)	7 812(11)	−661(8)
C(21)	6 494(13)	8 577(14)	−409(10)
C(22)	6 654(13)	8 757(13)	229(11)
C(23)	6 699(10)	8 073(11)	682(8)
C(24)	5 011(8)	4 781(8)	1 290(6)
C(25)	4 709(10)	5 525(10)	1 023(7)
C(26)	3 929(12)	5 780(11)	1 091(9)
C(27)	3 515(12)	5 311(12)	1 417(9)
C(28)	3 794(13)	4 564(13)	1 642(9)
C(29)	4 578(11)	4 265(10)	1 589(7)
C(30)	6 557(9)	3 521(9)	838(6)
C(31)	6 567(9)	2 717(9)	500(7)
C(32)	6 013(10)	2 099(10)	567(7)
C(33)	6 032(12)	1 297(12)	240(9)
C(34)	6 475(11)	1 225(11)	−181(9)
C(35)	7 069(10)	1 793(11)	−257(8)
C(36)	7 080(9)	2 579(9)	116(7)
C(37)	6 666(8)	3 772(8)	2 614(6)
C(38)	6 050(10)	4 031(10)	2 888(7)
C(39)	5 564(11)	3 452(11)	3 127(8)
C(40)	5 725(11)	2 623(11)	3 081(8)
C(41)	6 335(13)	2 366(12)	2 825(9)
C(42)	6 825(10)	2 928(11)	2 560(8)
C(43)	8 465(8)	4 737(8)	2 386(6)
C(44)	9 371(8)	4 655(8)	2 665(6)
C(45)	9 639(10)	3 880(10)	2 931(7)
C(46)	10 503(11)	3 738(11)	3 174(8)
C(47)	11 052(11)	4 358(12)	3 141(8)
C(48)	10 798(10)	5 128(11)	2 899(7)
C(49)	9 937(7)	5 290(7)	2 639(5)
P	2 260(5)	7 340(5)	2 292(5)
F(1)	2 299(11)	8 304(13)	2 292(9)
F(2)	1 352(13)	7 264(12)	2 272(9)
F(3)	2 407(12)	7 422(13)	3 048(10)
F(4)	2 237(12)	7 219(12)	1 577(10)
F(5)	2 270(11)	6 368(13)	2 302(8)
F(6)	3 209(11)	7 311(9)	2 325(7)

* C(11)–C(16), C(18)–C(23), C(24)–C(29), C(31)–C(36), C(37)–C(42) and C(44)–C(49) constitute the six benzene rings attached to N(3), C(17), N(6), C(30), N(9) and C(43) respectively.

IR spectra, Perkin-Elmer 783 spectrophotometer; magnetic susceptibility, PAR 155 vibrating-sample magnetometer; solution (10^{-3} mol dm^{-3}) electrical conductivities, Philips PR 9500 bridge; X-band ESR spectra, Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K (diphenylpicrylhydrazyl, g = 2.0037, used for calibration); microanalytical measurements (C,H,N), Perkin-Elmer 240C elemental analyser.

Preparations.—(Acetylacetonato)oxotris(μ-α-phenylazobenzaldehyde oximato)iron(II)*vanadium*(IV), [FeL$^1{}_3$VO(acac)]. To a solution of Na[FeL$^1{}_3$]·H$_2$O (400 mg, 0.52 mmol) in dichloromethane (25 cm^3) was added [VO(acac)$_2$] (140 mg, 0.52 mmol). The colour immediately changed from green to blue-green. The solution was then stirred at room temperature for 1 h followed by evaporation in air. The dark solid which precipitated was filtered off, washed thoroughly with ice-cold water and finally dried in vacuum over P_4O_{10}; yield 450 mg (97%). The complex [FeL$^2{}_3$VO(acac)] was similarly prepared in 94% yield.

(2,2′-Bipyridyl)oxotris(μ-α-phenylazobenzaldehyde oximato)-iron(II)*vanadium*(IV) *hexafluorophosphate*, [FeL$^1{}_3$VO(bipy)]PF$_6$. To a solution of [FeL$^1{}_3$VO(acac)] (400 mg, 0.45 mmol) in methanol (30 cm^3) was added aqueous 2 mol dm^{-3} HCl (2.3 cm^3) followed by 2,2′-bipyridine (bipy) (70 mg, 0.45 mmol) and excess (100 mg) of NH$_4$PF$_6$. The mixture was stirred at room temperature for 3 h. The precipitated dark solid was filtered off, washed thoroughly with ice-cold water and dried under vacuum over P_4O_{10}. It was then recrystallised from dichloromethane–hexane (1:1); yield 320 mg (65%).

All other complexes of type **2** were similarly prepared in similar yields.

X-Ray Structure Determination.—Crystals of [FeL$^1{}_3$VO(bipy)]PF$_6$ were grown by slow evaporation of dichloromethane–hexane (1:1).

Crystal data. $C_{49}H_{38}F_6FeN_{11}O_4PV$, M = 1096.7, monoclinic, space group $P2_1/n$, a = 16.607(2), b = 15.752(7), c = 21.242(3) Å, β = 104.65(1)°, U = 5376(2) Å^3 (by least-squares refinement of diffractometer angles for 25 machine-centred reflections having 2θ values in the range 15–35°), Z = 4, D_c = 1.355 g cm^{-3}, dark parallelopiped (0.40 × 0.28 × 0.18 mm), μ(Mo-Kα) = 5.36 cm^{-1}, λ = 0.710 73 Å, F(000) = 2236.

Data collection and processing. Nicolet R3m/V diffractometer, ω-scan method ($2 < 2\theta < 45°$; the crystal was weakly diffracting and few reflections with significant intensities occurred above 45°), graphite-monochromated Mo-Kα radiation; of the 7139 reflections collected 7064 were unique and 2704 observed [$F > 6\sigma(F)$]. The latter were corrected for Lorentz and polarisation factors, and a semiempirical absorption correction (transmission 0.807–0.839) was applied. Two standard reflections monitored showed no significant variations during 121 h exposure to X-rays.

Solution and refinement. The structure was solved by direct methods and subsequently refined by full-matrix least-squares procedures. Owing to the limited size of the observed data set, only iron, vanadium, nitrogen, oxygen and phosphorus atoms were made anisotropic. Hydrogen atoms were included at calculated positions (C–H 0.96 Å, U = 0.08 Å^2) in the final stage of refinement. Number of variables 384, affording a data-to-parameter ratio of 7.0:1. The refinement converged (maximum shift/e.s.d. 0.077) to a final R = 0.081, R' = 0.086 and goodness of fit = 2.08 with the largest difference peak and hole +0.43 and −0.47 e Å^{-3} respectively.

The quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F) + 0.0005(F)^2]$. Positional parameters for the non-hydrogen atoms are collected in Table 4. Computations were carried out on a MicroVAXII computer using the SHELXTL-PLUS program system.[30]

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

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References

1 J. A. Bonadies and C. J. Carrano, *J. Am. Chem. Soc.*, 1986, **108**, 4088.

2 X. Li, M. S. Lah and V. L. Pecoraro, *Inorg. Chem.*, 1988, **27**, 4567; C. J. Carrano, C. M. Nunn, R. Quan, J. A. Bonadies and V. L. Pecoraro, *Inorg. Chem.*, 1990, **29**, 944.

3 A. R. Bulls, C. G. Pippin, F. E. Halm and K. N. Raymond, *J. Am. Chem. Soc.*, 1990, **112**, 2627.

4 C. J. Dutton, G. D. Fallon and K. S. Murray, *J. Chem. Soc., Chem. Commun.*, 1990, 64.

5 S. G. Brand, N. Edelstein, C. J. Hawkins, G. Shalimoff, M. R. Snow and E. R. T. Tiekink, *Inorg. Chem.*, 1990, **29**, 434.

6 B. Kang, L. Weng, H. Liu, D. Wu, L. Huang, C. Lu, J. Cai, X. Chen and J. Lu, *Inorg. Chem.*, 1990, **29**, 4873.

7 U. Anerbach, B. S. P. C. D. Vedova, K. Wieghardt, N. Nuber and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1990, 1004.

8 T. A. Kabanos, A. D. Keramidas, D. Mentzafos and A. Terzis, *J. Chem. Soc., Chem. Commun.*, 1990, 1664.

9 P. Frank, R. M. K. Carlson and K. O. Hodgson, *Inorg. Chem.*, 1988, **27**, 118.

10 R. Wever and K. Kustin, *Adv. Inorg. Chem.*, 1990, **35**, 81; K. Kustin, G. C. McLeod, T. R. Gilbert and L. B. R. Briggs, *Struct. Bonding (Berlin)*, 1983, **53**, 139; N. D. Chasteen, *Struct. Bonding (Berlin)*, 1983, **53**, 107.

11 G. N. George, C. L. Coyle, B. J. Hales and S. P. Cramer, *J. Am. Chem. Soc.*, 1988, **110**, 4057; E. M. Oltz, R. C. Bruening, M. J. Smith, K. Kustin and K. Nakanishi, *J. Am. Chem. Soc.*, 1988, **110**, 6162.

12 W. R. Harris and C. J. Carrano, *J. Inorg. Biochem.*, 1984, **22**, 201.

13 H. Kneifel and E. Bayer, *J. Am. Chem. Soc.*, 1986, **108**, 3075.

14 E. deBoer, K. Boon and R. Wever, *Biochemistry*, 1988, **27**, 1629; H. Vitler, *Phytochemistry*, 1984, **23**, 1387; H. S. Soedjak and A. Butler, *Biochemistry*, 1990, **29**, 7974; *Inorg. Chem.*, 1990, **29**, 5015.

15 D. C. Crans, R. L. Bunch and L. A. Theisen, *J. Am. Chem. Soc.*, 1989, **111**, 7597; D. C. Crans, E. M. Willging and S. R. Butler, *J. Am. Chem. Soc.*, 1990, **112**, 427; D. C. Crans, R. A. Felty and M. M. Miller, *J. Am. Chem. Soc.*, 1991, **113**, 265.

16 J. A. Kovacs and R. H. Holm, *Inorg. Chem.*, 1987, **26**, 702, 711; *J. Am. Chem. Soc.*, 1986, **108**, 340; Y. Do, E. D. Simhon and R. H. Holm, *J. Am. Chem. Soc.*, 1983, **105**, 6731; *Inorg. Chem.*, 1985, **24**, 4635.

17 A. W. Rudie, D. W. Litchenberg, M. L. Kacher and A. Davison, *Inorg. Chem.*, 1978, **17**, 2859.

18 C. M. Bolinger, T. B. Rauchfuss and S. R. Wilson, *J. Am. Chem. Soc.*, 1982, **104**, 7313; T. B. Rauchfuss, T. D. Weatherhill, S. R. Wilson and J. P. Zebrowski, *J. Am. Chem. Soc.*, 1983, **105**, 6508; C. M. Bolinger, T. D. Weatherhill, A. L. Rheingold, C. S. Day and S. R. Wilson, *Inorg. Chem.*, 1986, **25**, 634.

19 B. S. R. Raghavendra, S. Gupta and A. Chakravorty, *Transition Met. Chem.*, 1979, **4**, 42.

20 S. Pal and A. Chakravorty, *Inorg. Chem.*, 1987, **26**, 4331.

21 S. Chattopadhyay, P. Basu, S. Pal and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1990, 3829 and refs. therein; P. Basu, S. Pal and A. Chakravorty, *Inorg. Chem.*, 1988, **27**, 1848.

22 S. Pal, T. Melton, R. N. Mukherjee, A. R. Chakravarty, M. Tomas, L. R. Falvello and A. Chakravorty, *Inorg. Chem.*, 1985, **24**, 1250.

23 S. Pal, R. N. Mukherjee, M. Tomas, L. R. Falvello and A. Chakravorty, *Inorg. Chem.*, 1986, **25**, 200.

24 B. K. Ghosh, R. N. Mukherjee and A. Chakravorty, *Inorg. Chem.*, 1987, **26**, 1946.

25 P. Basu, S. Pal and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1990, 9.

26 J. Zah-Letho, E. Samuel and J. Livage, *Inorg. Chem.*, 1988, **27**, 2233 and refs. therein.

27 K. C. Kalia and A. Chakravorty, *J. Org. Chem.*, 1970, **35**, 2231.

28 R. A. Rowe and M. M. Jones, *Inorg. Synth.*, 1957, **5**, 113.

29 P. J. Steel, F. Lahousse, D. Lerner and C. Margin, *Inorg. Chem.*, 1983, **22**, 1488.

30 G. M. Sheldrick, SHELXTL-PLUS 88, Structure Determination Software Programs, Nicolet Instrument Corp., Madison, 1988.

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