

**Synthesis and Crystal Structure of the New Dimeric Vanadyl  
Complex [V<sub>2</sub>O<sub>2</sub>(TPBN)(ACAC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.  
[TPBN = Tetrakis (2-pyridylmethyl)-1,4 -butanediamine]**

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A reação de [OV(ACAC)<sub>2</sub>] em solução metanólica com tetraquis (2- piridilmetil)-1,4-butano-diamina (TPBA) (estequiometria 2:1) fornece cristais violeta do dímero [V<sub>2</sub>O<sub>2</sub>(TPBN)(ACAC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (1). A estrutura cristalina do complexo 1 foi determinada por cristalografia de raios X e cristaliza-se no sistema triclinico, grupo espacial, P-1, [No. 2], com M<sub>r</sub> = 1074.64, e dimensões de cela a = 9.352(2), b = 9.783(1), c = 13.371(9) Å, α = 71.64(3), β = 80.29(3), γ = 84.30(2)<sup>o</sup>, V = 1143.0(8) Å<sup>3</sup>, Z = 1, D<sub>calc</sub> = 1.56 Mg m<sup>-3</sup>, λ = 0.70930 Å, μ = 0.561 mm<sup>-1</sup>, F(000) = 548, T = 296 K, R = 8.7% (R<sub>w</sub> = 8.6%), com 8949 reflexões medidas e 3997 observadas com I > 3σ(I). O ambiente de coordenação em torno do grupo VO<sup>2+</sup> é definido por dois átomos N-piridina e dois átomos de O de um acetilacetato bidentado no plano equatorial. Um átomo N-amina do ligante, TPBN em posição *trans* em relação ao grupo terminal oxo completa a esfera de coordenação.

The reaction of [OV(ACAC)<sub>2</sub>] in methanolic solution with tetrakis (2-pyridylmethyl)-1,4-butanediamine (TPBA) (stoichiometry 2:1), yields violet crystals of the dimeric [V<sub>2</sub>O<sub>2</sub>(TPBN)(ACAC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (1). The crystal structure of 1 has been determined by X-ray crystallography, 1 crystallizes in the triclinic space group P-1, [Nr 2], with M<sub>r</sub> = 1074.64, and cell dimensions a = 9.352(2), b = 9.783(1), c = 13.371(9) Å, α = 71.64(3), β = 80.29(3), γ = 84.30(2)<sup>o</sup>, V = 1143.0(8) Å<sup>3</sup>, Z = 1, D<sub>calc</sub> = 1.56 Mg m<sup>-3</sup>, λ = 0.70930 Å, μ = 0.561 mm<sup>-1</sup>, F(000) = 548, T = 296 K, R = 8.7% (R<sub>w</sub> = 8.6%), with 8949 measured reflections and 3997 observed reflections with I > 3σ(I). The coordination environment around the VO<sup>2+</sup> group is defined by two N-pyridyl and two O atoms of one bidentate acetylacetonate ligand in the equatorial plane. One N-amine atom of the TPBN ligand in the *trans* position with respect to the terminal oxo-group completes the coordination sphere.

**Keywords:** *vanadyl complex, X-ray crystal structure*

## Introduction

The chemistry of vanadium complexes has been the subject of extensive study over the past decade since vanadium is present at the active site of certain enzymes, including haloperoxidases in sea algae and lichens<sup>1</sup> and some nitrogenases in nitrogen-fixing *Azobacter*<sup>2</sup>. The complex amavadin from the mushroom *Amanita muscaria* was isolated and characterized in 1973, and while the function of this compound remains unknown, amavadin represents the first example of a vanadium coordination complex from a biological source that has been fully defined<sup>3</sup>. Furthermore, recent EXAFS results for the dithionite-reduced bromoperoxidase enzyme have been modeled by a short V = O distance of  $\sim 1.6$  Å, two or three nitrogen/oxygen ligands at  $\sim 1.90$  Å and two ligands at  $\sim 2.05$  Å<sup>4</sup>. Second shell modeling is suggestive of imidazole coordination<sup>4,5</sup>. Therefore, the synthesis and structural characterization of new vanadium complexes with relevant nitrogen and oxygen donor ligands is an important area of study. In this work, we report the preparation and X-ray crystal structure of such a complex. This is part of our program for the preparation and characterization of vanadium complexes with bioinorganic relevance<sup>6-8</sup>.

## Experimental

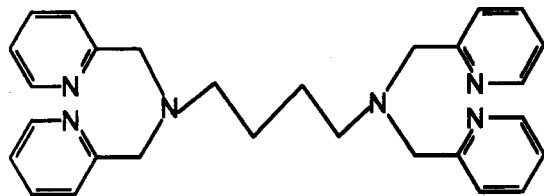
### Synthesis

The ligand tetrakis (2-pyridylmethyl)-1,4-butanediamine (TPBN) (Fig. 1), was prepared as described in the literature<sup>9</sup>.

$[V_2O_2(TPBN)(ACAC)_2](PF_6)_2$  (**1**).  $OV(ACAC)_2$  (0.53 g, 1.9 mmol) was added to a solution of TPBN (0.45 g, 1.0 mmol) in methanol (20 mL). The green solution was heated to 50 °C, and  $NH_4PF_6$  was added. After the solution was cooled to room temperature, a violet microcrystalline precipitate was observed which was collected by filtration, washed with cold ethanol and ether, and air dried. Crystals of **1** suitable for X-ray crystallography were obtained by slow evaporation of a methanol solution of the complex.

### X-ray crystallography

A violet crystal with approximate dimensions 0.35 x 0.15 x 0.25 mm was mounted on a glass fiber and placed on an Enraf-Nonius CAD-4 diffractometer. The unit cell dimensions and the orientation matrix for the data collec-



**Figure 1.** The ligand TPBN = tetrakis (2-pyridylmethyl)-1,4-butanediamine.

tion were obtained by a least-squares fit of 25 centered reflections ( $11.0 < \theta < 20.0^\circ$ ). Intensity data were measured by the  $\omega - 2\theta$  scan with graphite-monochromated  $MoK\alpha$  radiation, a scan speed of 4-20 deg/min and a scan range of  $(0.75 + 0.35 \tan\theta)$  deg. The intensities of three standard reflections were measured every 60 min. and varied less than 1.7%. The intensity data were corrected for Lorentz and polarization effects, but no decay correction was applied. The number of measured reflections was 8949 in the range of -11/11, -12/12, -16/16, with 4476 unique reflections. Equivalent reflections were merged with  $R_{int} = 1.96\%$ . Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. Assuming a density comparable to other vanadium complexes for which structures have been previously solved, we obtained  $Z = 1$ , consistent with the space group P1. However, the intensity statistics were consistent with a centrosymmetric space group. Therefore, we solved and successfully refined this structure in P-1, with the asymmetric unit as half a molecule, and the other half of the molecule was generated by the inversion symmetry operation.

The structure was solved by means of direct methods employing SHELXS86 programs<sup>10</sup> and subsequent Fourier difference synthesis. The DIFABS<sup>11</sup> absorption correction was applied after isotropic refinement with  $T_{min} = 0.889$ ,  $T_{max} = 1.041$  and  $T_{aver.} = 0.965$ . The structure was refined by full-matrix least-squares techniques which minimized  $\Sigma w(\Delta F)^2$ :  $w = 1/[\sigma(F_o)]^2$ . The positions of the hydrogen atoms were calculated and included in the final refinement using the VAXSDP (version 3.0) package programs<sup>12</sup>. All non-hydrogen atoms were refined with the use of anisotropic thermal parameters. At the end of the refinement an isotropic extinction correction with a coefficient  $g = 1.37 \times 10^{-2}$  was applied. The number of refined parameters was 298, and the fit was 1.38. Residual densities of 2.40 and  $2.16 e / \text{\AA}^{-3}$  in the final difference map were located in the  $PF_6$  area, at distances of 1.026 Å and 1.038 Å from the F5 and F6 atoms respectively, indicating some disorder. Some attempts to model this disordered  $PF_6$  group were unsuccessful. The final refinement gave  $R = 0.087$ ,  $R_w = 0.086$ , and all parameter shifts were less than 0.10 of the corresponding standard deviations.

The calculations were carried out on a VAX computer at the University of Tübingen, but the ORTEP drawing<sup>13</sup> and some tables were done at the Universidade Federal de Santa Catarina, Brazil.

## Results and Discussion

Crystals of **1** consist of the dimeric dication  $[V_2O_2(TPBN)(ACAC)_2]^{2+}$  and uncoordinated hexafluorophosphate anions in general positions. An ORTEP drawing of the dication with an atom-labeling scheme is shown in Fig.

2. The atomic parameters, bond distances and angles are given in Tables 1, 2 and 3, respectively. The dication in **1** has an inversion center between the C4 and C4' carbon atoms. The molecule consists of two six coordinate vanadium (IV) centers in which an individual TPBN ligand donates three nitrogen atoms in a facial arrangement to each

independent vanadyl ( $\text{VO}^{2+}$ ) group; an additional bidentate acetylacetonate ligand completes the coordination sphere at each vanadium center. Interestingly, the substitution of the 1,4-butane group in TPBN by a shorter saturated carbon chain  $[-(\text{CH}_2)-]$ , as in tetrakis [2-pyridylmethyl ethylenediamine (TPEN)]<sup>14</sup>, leads to a situation where the binucleating ligand TPEN encompasses two  $\mu$ -hydroxo bridged vanadyl ions and the  $\text{V} = \text{O}$  groups are in *syn*-configuration. The vanadium ion in **1** lies in a highly distorted octahedral environment with the V center being displaced above the equatorial plane by 0.065 Å towards the oxo ligand. As expected, the  $\text{V}-\text{N}_{(\text{amine})}$  bond distance of 2.351(2) Å *trans* to the  $\text{V}=\text{O}$  bond [1.585(3) Å] is significantly longer ( $\sim 0.22$  Å) than the two  $\text{V}-\text{N}_{(\text{pyridine})}$  distances (av. 2.127(3) Å) and is a reflection of the strong *trans* influence of the oxo group<sup>8,14</sup>.  $\text{V}-\text{N}_{(\text{amine})}$  and  $\text{V}-\text{N}_{(\text{pyridine})}$  distances in the equatorial plane of vanadyl complexes and *trans* to donor atoms of the same nature, differ slightly ( $\sim 0.05$  Å)<sup>8</sup>. Moreover, the double bond character of the V-oxo group may be confirmed by the infrared spectrum of **1**. An intense band at 988  $\text{cm}^{-1}$  was assigned to the stretching vibration due to  $\nu(\text{V} = \text{O})$ <sup>11</sup>.

The coordination geometry and dimensions of the bidentate ACAC ligand in the equatorial plane of **1** are very similar to those observed in other vanadyl-ACAC complexes<sup>16-18</sup>; the six-membered chelate ring is closely planar and the V-O distances [av. 1.991(2) Å] in **1** compare very well with those detected in  $[\text{V}_2(\text{VO})_2(\text{ACAC})_4(\text{CH}_3\text{O})_6]$  [av. 1.989(5) Å]<sup>18</sup> and  $[\text{V}_2\text{O}(\text{ACAC})_2(\text{dioxane})]$  (1.99

**Table 1.** Final positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses.

Atom	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
V	0.36190(8)	0.88200(7)	0.19885(5)	3.93(1)
O1	0.4652(3)	0.9307(3)	0.3014(2)	4.41(7)
O2	0.3094(3)	1.0906(3)	0.1420(2)	4.51(7)
O3	0.4938(4)	0.8557(4)	0.1144(3)	6.10(9)
N1	0.1422(3)	0.8626(3)	0.3163(2)	2.91(6)
N11	0.3686(3)	0.6664(3)	0.3025(2)	3.59(7)
N21	0.2023(4)	0.8419(3)	0.1170(2)	4.26(8)
C1	0.0289(4)	0.9243(4)	0.2453(3)	3.47(8)
C2	0.1185(4)	0.7070(4)	0.3721(3)	3.29(7)
C3	0.1396(4)	0.9448(4)	0.3933(3)	3.01(7)
C4	-0.0075(4)	0.9632(4)	0.4589(2)	3.03(7)
C12	0.2565(4)	0.6182(4)	0.3785(3)	3.25(7)
C13	0.2648(5)	0.4849(4)	0.4553(3)	4.38(9)
C14	0.3902(5)	0.3997(5)	0.4528(4)	5.4(1)
C15	0.5041(5)	0.4485(5)	0.3734(4)	5.5(1)
C16	0.4906(5)	0.5823(5)	0.3012(4)	4.7(1)
C22	0.0621(5)	0.8662(4)	0.1513(3)	4.15(9)
C23	-0.0498(5)	0.8424(5)	0.1014(3)	5.2(1)
C24	-0.0057(6)	0.7939(5)	0.0126(3)	6.6(1)
C25	0.1360(7)	0.7714(5)	-0.0228(3)	6.9(1)
C26	0.2374(7)	0.7962(5)	0.0318(3)	6.0(1)
C31	0.6208(6)	1.0494(6)	0.3618(5)	7.8(2)
C32	0.5165(4)	1.0520(5)	0.2866(4)	5.2(1)
C33	0.4820(5)	1.1797(5)	0.2128(4)	5.7(1)
C34	0.3782(5)	1.1946(5)	0.1460(4)	5.3(1)
C35	0.3396(6)	1.3406(5)	0.0721(5)	6.8(2)
P	0.9372(1)	0.4040(1)	0.26461(9)	4.36(2)
F1	0.8620(3)	0.5471(3)	0.2877(3)	7.10(8)
F2	1.0079(5)	0.2655(3)	0.2395(3)	8.8(1)
F3	0.8035(5)	0.4075(5)	0.2058(3)	13.8(1)
F4	1.0455(5)	0.3902(5)	0.3403(4)	13.6(1)
F5	0.8398(4)	0.3121(4)	0.3676(3)	9.1(1)
F6	1.0258(5)	0.4937(4)	0.1689(4)	21.4(1)

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

**Table 2.** Bond lengths (Å), with e.s.d.'s in parentheses.

V	O1	1.998(3)	C1	C22	1.512(4)
V	O2	1.984(2)	C2	C12	1.482(4)
V	O3	1.585(3)	C3	C4	1.529(4)
V	N1	2.351(2)	C12	C13	1.387(5)
V	N11	2.129(3)	C13	C14	1.371(5)
V	N21	2.126(3)	C14	C15	1.376(6)
O1	C32	1.268(4)	C15	C16	1.369(6)
O2	C34	1.276(5)	C22	C23	1.405(5)
N1	C1	1.497(4)	C23	C24	1.398(6)
N1	C2	1.489(4)	C24	C25	1.351(7)
N1	C3	1.489(4)	C25	C26	1.372(7)
N11	C12	1.338(4)	C31	C32	1.508(6)
N11	C16	1.340(4)	C32	C33	1.374(6)
N21	C22	1.338(5)	C33	C34	1.395(6)
N21	C26	1.330(4)	C34	C35	1.509(6)
P	F1	1.598(2)	P	F4	1.522(5)
P	F2	1.555(3)	P	F5	1.579(4)
P	F3	1.578(5)	P	F6	1.474(5)

Å)<sup>16</sup>. The two remaining five-membered rings formed by the 2-pyridylmethyl groups are rigid and deviate from relative planarity. The sum of the interior angles are 533.6° and 522.0° for the N11-V-N1-C2-C12 and N21-V-N1-C22

rings, respectively. A more detailed analysis of the torsion angles within the two ring arms gives the extent of puckering in the inner and outer regions of these rings in molecule 1. The torsion angles are N11-V-N1-C2 = 15.2° and V-

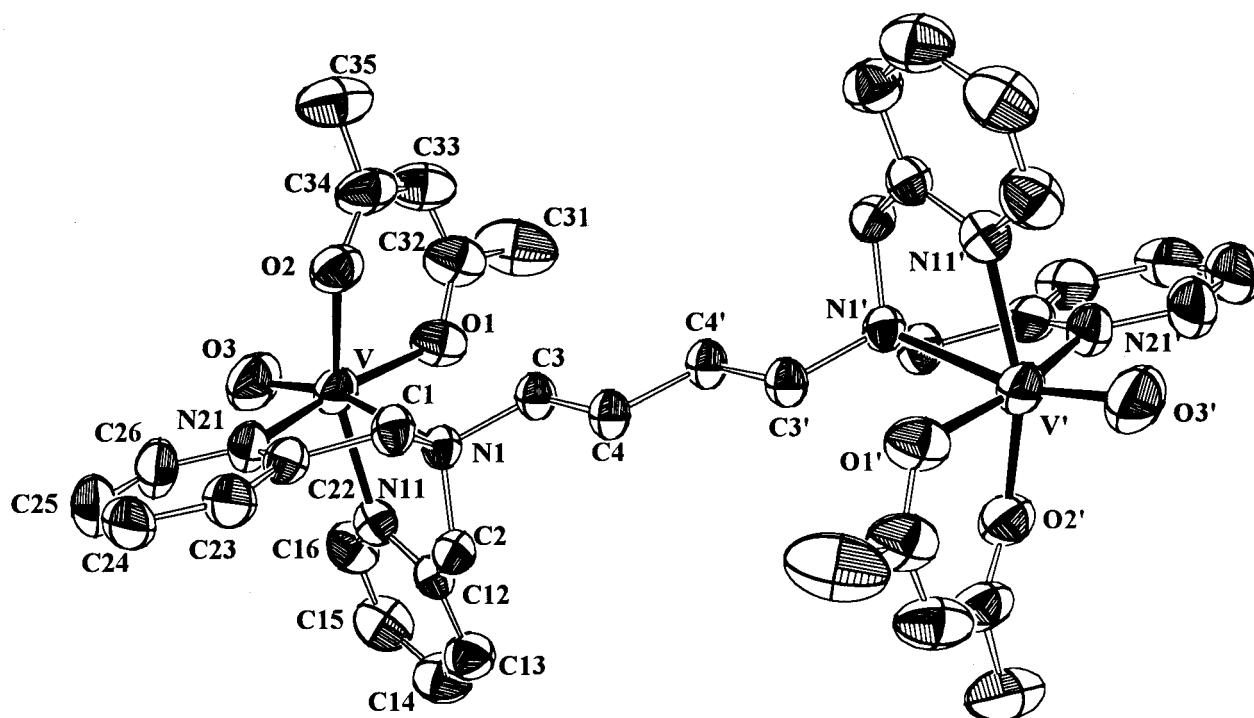


Figure 2. ORTEP of the structure of the cation of 1, showing the atom-labeling scheme.

Table 3. Bond angles (°), with e.s.d.'s in parentheses

O1	V	O2	87.7(2)	V	N11	C16	120.7(2)	V	O2	C34	126.5(3)	C22	C23	C24	115.9(4)
O1	V	O3	101.4(1)	C12	N11	C16	118.5(4)	V	N1	C1	104.3(2)	C23	C24	C25	121.9(4)
O1	V	N1	91.2(1)	V	N21	C22	118.7(2)	V	N1	C2	108.6(2)	C24	C25	C26	118.0(4)
O1	V	N11	86.0(2)	V	N21	C26	122.2(3)	V	N1	C3	112.2(2)	O1	C32	C31	114.1(4)
O1	V	N21	164.7(2)	C22	N21	C26	119.1(4)	C1	N1	C2	109.6(2)	O1	C32	C33	126.2(5)
O2	V	O3	103.6(1)	N1	C1	C22	108.2(3)	C1	N1	C3	110.5(2)	C31	C32	C33	119.7(4)
O2	V	N1	87.44(9)	N1	C2	C12	112.3(3)	C2	N1	C3	111.5(2)	C32	C33	C34	123.7(4)
O2	V	N11	161.3(2)	N1	C3	C4	116.2(2)	V	N11	C12	120.3(2)	C33	C34	C35	120.5(4)
O2	V	N21	87.9(1)	N11	C12	C2	117.3(3)	F1	P	F2	178.4(2)	F3	P	F4	169.1(2)
O3	V	N1	163.4(1)	C2	C12	C13	120.9(3)	F1	P	F3	85.6(2)	F3	P	F5	85.4(2)
O3	V	N11	94.9(1)	C12	C13	C14	119.4(4)	F1	P	F4	91.7(2)	F3	P	F6	94.4(3)
O3	V	N21	93.9(1)	C13	C14	C15	118.9(4)	F1	P	F5	88.8(2)	F4	P	F5	84.0(2)
N1	V	N11	75.09(9)	C14	C15	C16	119.0(4)	F1	P	F6	89.5(2)	F4	P	F6	96.2(3)
N1	V	N21	73.9(1)	N11	C16	C15	122.6(4)	F2	P	F3	92.9(2)	F5	P	F6	178.3(2)
N11	V	N21	93.5(2)	N21	C22	C1	116.8(3)	F2	P	F4	89.9(4)				
V	O1	C32	125.0(3)	C1	C22	C23	121.0(4)	F2	P	F5	91.6(2)				

$N11-C12-C2 = -13.3^\circ$ ;  $N21-V-N1-C1 = 33.8^\circ$  and  $V-N21-C22-C1 = -1.4^\circ$ .

The  $PF_6^-$  anion does not show any interaction with the cationic complex of **1**. In summary, a new synthetic vanadyl model complex with V-O and V-N distances similar to those established by EXAFS studies in reduced bromoperoxidase has been synthesized and structurally characterized. Moreover, the pyridyl groups in TPBN are

biomimetic ligands for imidazole, a probable donor in this metalloenzyme.

The remaining structural parameters for the ligand are as expected and will not be further discussed.

### Supplementary Material

The list of the observed and calculated structure factors (33 p.), anisotropic thermal parameters (Table 4) and hy-

**Table 4.** Anisotropic thermal parameters.

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
V	0.0504(4)	0.0501(3)	0.0434(3)	-0.0043(3)	0.0074(3)	0.0131(2)
O1	0.039(1)	0.055(1)	0.073(2)	-0.009(1)	-0.004(1)	-0.020(1)
O2	0.056(2)	0.050(1)	0.056(1)	-0.006(1)	0.005(1)	-0.009(1)
O3	0.079(2)	0.077(2)	0.061(2)	-0.003(2)	0.018(2)	-0.015(1)
N1	0.041(1)	0.041(1)	0.030(1)	-0.003(1)	-0.008(1)	-0.011(1)
N11	0.047(2)	0.045(1)	0.046(1)	-0.000(1)	-0.007(1)	-0.018(1)
N21	0.078(2)	0.049(2)	0.033(1)	0.000(2)	-0.006(1)	-0.013(1)
C1	0.048(2)	0.050(2)	0.035(1)	0.001(2)	-0.015(1)	-0.012(1)
C2	0.044(2)	0.044(2)	0.036(2)	-0.006(1)	-0.002(1)	-0.012(1)
C3	0.034(2)	0.048(2)	0.036(1)	-0.003(1)	-0.006(1)	-0.016(1)
C4	0.033(2)	0.050(2)	0.035(1)	-0.002(1)	-0.006(1)	-0.016(1)
C12	0.045(2)	0.044(2)	0.038(1)	-0.005(1)	-0.010(1)	-0.017(1)
C13	0.060(2)	0.052(2)	0.054(2)	-0.005(2)	-0.013(2)	-0.012(2)
C14	0.072(3)	0.051(2)	0.077(3)	0.007(2)	-0.024(2)	-0.011(2)
C15	0.060(3)	0.061(2)	0.088(3)	0.014(2)	-0.020(2)	-0.026(2)
C16	0.051(2)	0.060(2)	0.072(2)	0.004(2)	-0.006(2)	-0.027(2)
C22	0.081(2)	0.043(2)	0.035(2)	-0.008(2)	-0.022(2)	-0.005(1)
C23	0.103(3)	0.054(2)	0.047(2)	-0.014(2)	-0.042(2)	-0.005(2)
C24	0.155(4)	0.053(2)	0.051(2)	-0.021(2)	-0.053(2)	-0.006(2)
C25	0.157(5)	0.066(3)	0.043(2)	-0.004(3)	-0.023(3)	-0.020(2)
C26	0.125(4)	0.064(2)	0.037(2)	0.003(3)	-0.008(2)	-0.019(2)
C31	0.065(3)	0.084(3)	0.160(4)	-0.017(2)	-0.047(3)	-0.033(3)
C32	0.037(2)	0.067(2)	0.093(3)	-0.015(2)	0.004(2)	-0.027(2)
C33	0.054(2)	0.058(2)	0.103(3)	-0.018(2)	-0.005(2)	-0.017(2)
C34	0.056(2)	0.049(2)	0.077(3)	-0.010(2)	0.023(2)	-0.010(2)
C35	0.074(3)	0.055(3)	0.108(4)	-0.011(2)	0.009(3)	-0.005(3)
P	0.0668(6)	0.0469(5)	0.0547(5)	-0.0043(5)	-0.0116(5)	0.0172(4)
F1	0.085(2)	0.065(1)	0.122(2)	-0.007(1)	-0.002(2)	-0.038(1)
F2	0.180(3)	0.063(2)	0.091(2)	0.026(2)	-0.022(2)	-0.030(1)
F3	0.210(3)	0.209(3)	0.171(2)	0.080(3)	-0.129(2)	-0.127(2)
F4	0.143(3)	0.171(3)	0.258(3)	0.016(2)	-0.120(2)	-0.100(2)
F5	0.104(2)	0.090(2)	0.124(3)	0.002(2)	-0.008(2)	0.004(2),
F6	0.281(3)	0.083(2)	0.254(3)	0.069(2)	0.215(2)	0.069(2)

**Table 5.** Final positional parameters and equivalent isotropic temperature factors of hydrogen atoms.

Atom	x	y	z	B(A <sup>2</sup> )
H11	0.0291	1.0274	0.2218	5.0*
H12	-0.0658	0.8974	0.2836	5.0*
H13	0.1823	0.4524	0.5097	5.0*
H14	0.3989	0.3074	0.5067	5.0*
H15	0.5921	0.3890	0.3686	5.0*
H16	0.5725	0.6183	0.2468	5.0*
H21	0.0580	0.6728	0.3347	5.0*
H22	0.0687	0.6964	0.4426	5.0*
H23	-0.1527	0.8586	0.1278	5.0*
H24	-0.0788	0.7754	-0.0244	5.0*
H25	0.1650	0.7397	-0.0848	5.0*
H26	0.3403	0.7793	0.0075	5.0*
H31	0.1727	1.0390	0.3542	5.0*
H32	0.2064	0.8972	0.4416	5.0*
H41	-0.0456	0.8702	0.4946	5.0*
H42	-0.0730	1.0191	0.4125	5.0*
H311	0.7146	1.0777	0.3245	5.0*
H312	0.5859	1.1139	0.4033	5.0*
H313	0.6313	0.9544	0.4110	5.0*
H331	0.5315	1.2640	0.2076	5.0*
H351	0.3011	1.4067	0.1110	5.0*
H352	0.4218	1.3812	0.0227	5.0*
H353	0.2659	1.3332	0.0314	5.0*

Starred atoms were refined isotropically.

drogen atom coordinates (Table 5) are available from the authors (I.V.) upon request.

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