References

Biagini Cingi, M., Bandoli, G., Clemente, D. A. & Tiripicchio, A. (1980). *J. Appl. Cryst.* **13**, 197–198.

Ciccarese, A., Clemente, D. A., Fanizzi, F. P., Marzotto, A. & Valle, G. (1998*a*). *Inorg. Chim. Acta*, **275–276**, 410–418.

Ciccarese, A., Clemente, D. A., Fanizzi, F. P., Marzotto, A. & Valle, G. (1998*b*). *Inorg. Chim. Acta*, **275–276**, 419–426.

Connick, W. B. & Gray, H. B. (1994). *Acta Cryst.* C**50**, 1040–1042.

Dhara, S. C. (1970). *Indian J. Chem.* **8**, 193–194.

Hempel, A., Camerman, N. & Camerman, A. (1982). *J. Am. Chem. Soc.* **104**, 3453–3456.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kowallick, R., Neuburger, M., Zehnder, M. & Kaden, T. A. (1997). *Helv. Chim. Acta*, **80**, 948–959.

Marzotto, A., Clemente, D. A. & Valle, G. (1997). *Acta Cryst.* C**53**, 1580–1583.

Marzotto, A., Clemente, D. A. & Valle, G. (1998). *Acta Cryst.* C**54**, 27–29.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659–660.

Niemeyer, H. M. (1979). *J. Mol. Struct.* **57**, 241–244.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Oksanen, A., Kivekäs, R., Lumme, P., Valkonen, J. & Laitalainen, T. (1989). *Acta Cryst.* C**45**, 1493–1495.

Raudaschl-Siebert, G., Lippert, B., Britten, J. F. & Beauchamp, A. L. (1986). *Inorg. Chim. Acta*, **124**, 213–217.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Visona', J. C. (1998). Thesis, University of Padova, Italy.

Wade, P. W., Hancock, R. D., Boeyens, C. A. & Dobson, S. M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 483–488.

Acta Cryst. (1998). C**54**, 1781–1784

Vanadyl Tetrakis(pentafluorophenyl)porphyrin Dichloromethane Solvate

Hugues Duval, Véronique Bulach, Jean Fischer and Raymond Weiss

Laboratoire de Cristallochimie et Chimie Structurale, UMR 7513, Université Louis Pasteur, Institut Le Bel, 4, rue Blaise Pascal, 67070 Strasbourg CEDEX, France. E-mail: fischer@chimie.u-strasbg.fr

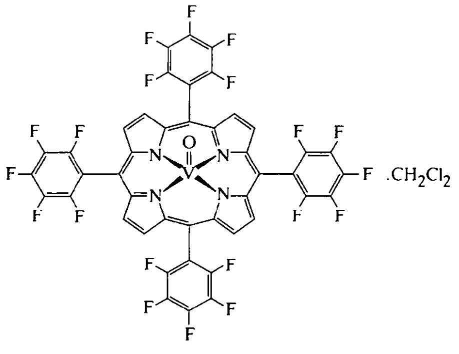
(*Received 13 February 1998; accepted 8 June 1998*)

Abstract

The vanadyl complex oxo[5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato-κ^4N]vanadium(IV) dichloromethane solvate, $[VO(C_{44}H_8F_{20}N_4)].CH_2Cl_2$, crystallizes in the monoclinic space group $P2_1/c$, with four molecules per unit cell. The V atom is found to lie 0.5237 (5) Å above the mean plane of the porphyrin core. The average V—N distance is 2.067 (5) Å and the V=O bond length is 1.585 (2) Å. The doming of the porphyrin core is characteristic of five-coordinate metalloporphyrins. Moreover, the macrocycle is slightly saddle-shaped and ruffled. Van der Waals contacts between the phenyl rings and the solvent molecules lead to dihedral angles between these phenyl rings and the porphyrin core mean plane ranging from 58.23 (5) to 89.38 (6)°. These contacts could explain the deviation of the porphyrin geometry relative to the fourfold symmetry.

Comment

The vanadyl complex of the title *meso*-pentafluorophenylporphyrin, VO(TPFPP), was synthesized quantitatively by reacting an excess of $VO(acac)_2$ (acac = acetylacetonate) with the porphyrin free base at 573 K. Single crystals of $[VO(TPFPP)].CH_2Cl_2$, (I), were obtained by slow diffusion of *n*-hexane into a solution of VO(TPFPP) in CH_2Cl_2 at room temperature. The complex (Fig. 1) crystallizes in the $P2_1/c$ space group with four molecules per unit cell.



(I)

The V^{IV} atom is five-coordinate, being bonded to the four pyrrole N atoms, N_p, of the porphyrin, and to one terminal oxo group. The metal geometry is close to square pyramidal. The V atom is displaced 0.5237 (5) Å from the mean plane of the porphyrin core towards the axially bonded O atom. This out-of-plane displacement lies in the range of 0.48–0.72 Å predicted by extended Huckël molecular-orbital calculations (Zerner & Gouterman, 1966). The V=O bond length of 1.585 (2) Å and the average V—N distance of 2.067 (5) Å are similar to those found in other vanadyl porphyrins (Molinaro & Ibers, 1976; Miller *et al.*, 1984; Drew *et al.*, 1984), *e.g.* 1.620 (2) and 2.102 (6) Å, respectively, in VO(OEP) (OEP = octaethylporphyrinato; Molinaro & Ibers, 1976). The V=O bond is tilted by 3.3 (1)° with respect to the normal to the porphyrin mean plane.

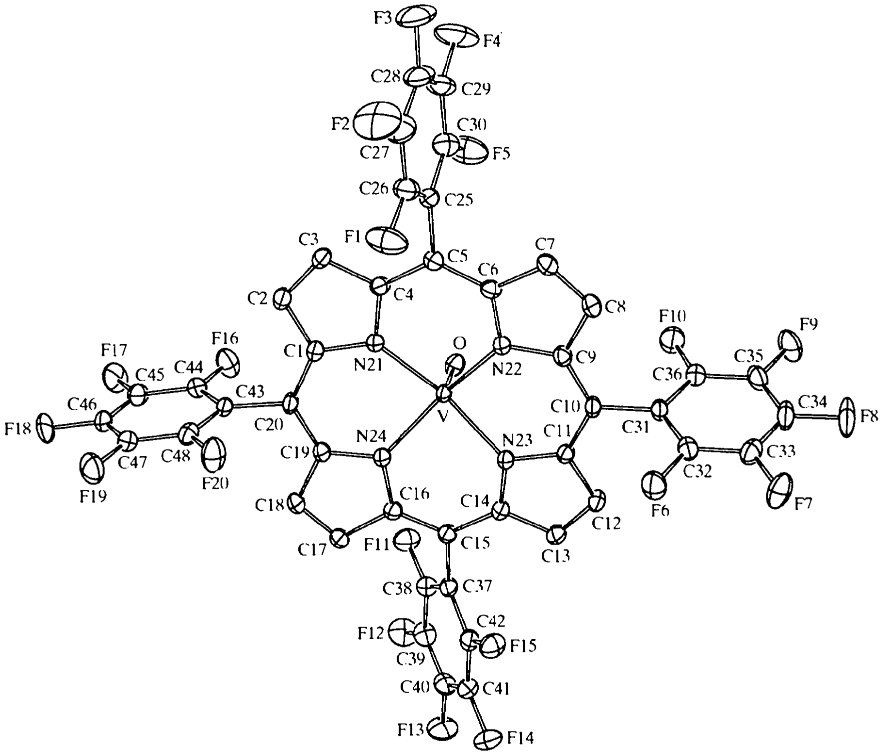


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the VO(TPFPP) molecule showing the atom labels. Ellipsoids are scaled to enclose 50% of the electron density.

A formal diagram displaying the deviation of each atom (in units of 0.01 Å) from the mean plane of the porphyrin core in VO(TPFPP) is given in Fig. 2. A comparison of this structure with that of the free base H_2TPFPP (Birnbaum *et al.*, 1995) shows that the exchange of H_2 for VO has minimal effect on the bond lengths of the porphyrin core. Of course, the porphyrin core is far less planar in the complex; the slight doming which is characteristic of five-coordinate metalloporphyrins is observed. Moreover, the 24 atoms of the porphyrin core are readily displaced in a direction perpendicular to the mean plane of the macrocycle, leading to a deviation of the porphyrin geometry relative to the fourfold symmetry. The pyrrole rings are quasi-planar. The C_β—C_β bonds are alternatively above and below the mean plane of the 24 core atoms (see Fig. 2), and hence the conformation of the macrocycle is slightly saddle-shaped. The maximum deviations from the porphyrin mean plane are −0.256 (3) Å for C18, and 0.200 (3) Å for C13.

The *meso* C atoms are also alternately above and below the core mean plane, but the ruffling is small. Indeed, the average displacement (absolute values) of the C_{meso} atoms from the mean plane of the porphyrin ring is 0.08 Å, and the dihedral angles between the pyrrole rings and the mean plane of the porphyrin core range from 2.1 to 7.2°. This ruffling is similar to that observed in VO(OEP) (Molinaro & Ibers, 1976).

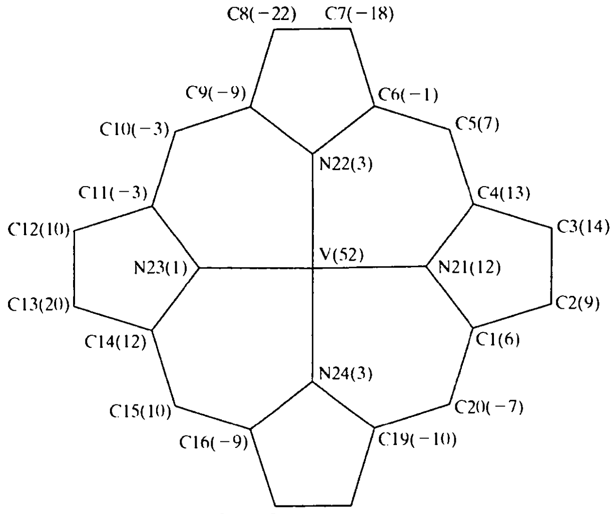


Fig. 2. Perpendicular deviation of each atom (in units of 0.01 Å) from the mean plane of the 24 core atoms of the porphyrin system in VO(TPFPP).

The C_α—C_{meso}—C_{phenyl} angles are close to 120°, but the phenyl rings bonded to C5 (Ph1), C10 (Ph2), C15 (Ph3) and C20 (Ph4) form dihedral angles with the porphyrin mean plane of 75.29 (7), 72.98 (7), 58.23 (5) and 89.38 (6)°, respectively. A packing drawing shows that the solvent molecules are located close to the phenyl rings, especially to Ph3. Hence, several distances between CH_2Cl_2 and the F atoms of Ph3 are less than the van der Waals distances. These contacts could explain the small dihedral angles between Ph3 and the mean plane of the porphyrin core. Indeed, compounds for which the dihedral angles between the phenyl rings and the porphyrin core mean plane are small, usually have a saddle-shaped deformation (Scheidt & Lee, 1987). For comparison, we have obtained single crystals of [VO(TPFPP)].$0.5H_2O.0.5CHCl_3$ by slow diffusion of *n*-heptane into a solution of VO(TPFPP) in $CHCl_3$. The data were collected at room temperature, but the complex decomposed during data collection and therefore the quality of the structure is poor. However, preliminary results showed that this complex crystallizes in the monoclinic space group $P2_1/n$. In this complex, the macrocycle is also domed and slightly ruffled, but not saddle-shaped. Moreover, the dihedral angles between the phenyl rings and the mean plane of the 24 core atoms range from 67.1 (2) to 83.5 (2)° and there are several contacts between solvent molecules and phenyl rings.

It is not clear whether the saddle-shaped deformation and the ruffling of [VO(TPFPP)].CH_2Cl_2 are due solely to the crystal packing, but the difference between the two structures, *i.e.* [VO(TPFPP)].CH_2Cl_2 and [VO(TPFPP)].$0.5H_2O.0.5CHCl_3$, emphasizes the strong influence of the packing forces on the deformation of the porphyrin ring.

Experimental

The title compound was prepared by adapting the procedures described by Buchler *et al.* (1971) and Schulz *et al.* (1994) for the preparation of VO(OEP). VO(TPFPP) was obtained quantitatively by reacting a pulverized mixture of porphyrin free base (H_2TPFPP; 0.20 g, 0.2 mmol) and VO(acac)$_2$ (0.27 g, 5 equivalents) in a test tube. The tube was heated for 1 h at 573 K in a Woods metal bath. After cooling to room temperature, the black residue was dissolved in 100 ml of CH_2Cl_2 and filtered through a medium frit. The solution was chromatographed on a silica-gel column by eluting with CH_2Cl_2/hexane (3/1). The first fraction was collected and evaporated. The resulting pink solid was recrystallized from CH_2Cl_2/hexane. UV–visible (CH_2Cl_2), λ (nm): 415 (Soret band), 541, 577. Single crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a solution of VO(TPFPP) in CH_2Cl_2.

Crystal data

$[VO(C_{44}H_8F_{20}N_4)].CH_2Cl_2$
$M_r = 1124.42$
Monoclinic
$P2_1/c$
$a = 14.070\,(2)$ Å
$b = 11.328\,(2)$ Å
$c = 26.375\,(3)$ Å
$\beta = 101.458\,(9)°$
$V = 4119\,(1)$ Å^3
$Z = 4$
$D_x = 1.81$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18.5–25.1°$
$\mu = 0.507$ mm^{-1}
$T = 173$ K
Prism
0.50 × 0.45 × 0.40 mm
Dark blue

Data collection

Enraf–Nonius MACH3 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.767$, $T_{\max} = 0.816$
10 108 measured reflections
9900 independent reflections

6504 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 27.47°$
$h = -18 \rightarrow 17$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 34$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.046$
$wR = 0.072$
$S = 1.479$
6504 reflections
658 parameters
H-atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0064F_o^4]$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.913$ e Å^{-3}
$\Delta\rho_{\min} = -0.109$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

V—O	1.585 (2)	V—N23	2.060 (2)
V—N21	2.071 (2)	V—N24	2.068 (2)
V—N22	2.068 (2)		
O—V—N21	104.5 (1)	N21—V—N23	154.4 (1)
O—V—N22	103.1 (1)	N21—V—N24	86.68 (9)
O—V—N23	101.1 (1)	N22—V—N23	87.59 (9)
O—V—N24	104.7 (1)	N22—V—N24	152.2 (1)
N21—V—N22	86.93 (9)	N23—V—N24	86.6 (1)

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1004). Services for accessing these data are described at the back of the journal.

References

Birnbaum, E. R., Hodge, J. A., Grinstaff, M. W., Schaefer, W. P., Henling, L., Labinger, J. A., Bercaw, J. E. & Gray, H. B. (1995). *Inorg. Chem.* **34**, 3625–3632.

Buchler, J. W., Eikelmann, G., Pupp, L., Rohbock, K., Schneehage, H. H. & Weck, D. (1971). *Liebigs Ann. Chem.* **745**, 135–151.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Drew, M. G. B., Mitchell, P. C. H. & Scott, C. E. (1984). *Inorg. Chim. Acta*, **82**, 63–68.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Miller, S. A., Hambley, T. W. & Taylor, J. C. (1984). *Aust. J. Chem.* **37**, 761–766.
Molinaro, F. S. & Ibers, J. A. (1976). *Inorg. Chem.* **15**, 2278–2283.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Scheidt, W. R. & Lee, Y. (1987). *Struct. Bonding*, **64**, 1–70.
Schulz, C. E., Song, H., Lee, Y. J., Mondal, J. U., Mohanrao, K., Reed, C. A., Walker, F. A. & Scheidt, W. R. (1994). *J. Am. Chem. Soc.* **116**, 7196–7203.
Zerner, M. & Gouterman, M. (1966). *Inorg. Chem.* **5**, 1699–1706.

Acta Cryst. (1998). C**54**, 1784–1787

Metal Alkoxycarboxylate Complexes. II. Poly[diaquabis(3-hydroxypropionato)-yttrium(III)] Bromide and *catena*-Poly-[pentaaqua(3-hydroxypropionato)-yttrium(III)] Bromide Chloride

Joel T. Mague, Allen W. Apblett and Galina Todorova

Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. E-mail: joelt@mailhost.tcs.tulane.edu

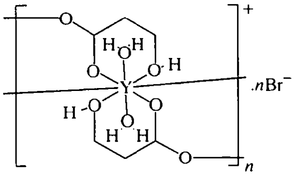
(*Received 6 April 1998; accepted 14 July 1998*)

Abstract

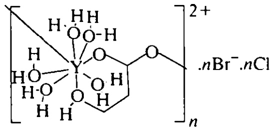
Poly[diaquayytrium(III)bis(μ-3-hydroxypropionato-O^3,-O^1:$O^{1'}$) bromide], $\{[Y(O_2CCH_2CH_2OH)_2(H_2O)_2]Br\}_n$, forms a layer structure consisting of sheets of cations in which the 3-hydroxypropionate ligands chelate to one metal *via* the hydroxyl and one carboxyl O atom, and bridge to adjacent metals *via* the second carboxyl O atom. The same chelating/bridging coordination of the carboxylate ligand occurs in *catena*-poly[[pentaaquayttrium(III)]-μ-(3-hydroxypropionato-O^3,O^1:$O^{1'}$) bromide chloride], $\{[Y(O_2CCH_2CH_2OH)(H_2O)_5](Br)Cl]\}_n$, to give cation chains which are arranged in layers. In both structures, the anions lie between the cation units and hold the latter together *via* hydrogen bonding.

Comment

Metal carboxylates decomposing at low temperatures to the corresponding oxide and volatile organic fragments are promising candidates for ceramic preparation by metallo-organic deposition (Apblett & Georgieva, 1994; Apblett *et al.*, 1992, 1997). This is particularly true if they melt below the decomposition point as this permits processing into thin films without the need for solvent. Such species could also be precursors for ceramic foams if the pyrolysis produces copious quantities of gas. In this context, metal 3-hydroxypropionates are of considerable interest since they tend to have low melting points (the sodium and calcium salts melt in the range 413–418 K) and decompose to ethylene, carbon dioxide and the metal oxide. In addition, 3-hydroxypropionic acid and its salts are important in biological and environmental systems. For example, a novel autotrophic carbon dioxide fixation pathway involving 3-hydroxypropionate was identified in the phototrophic bacterium *Chloroflexus aurantiacus* (Straus & Fuchs, 1993), while 3-hydroxypropionate is a metabolite of the herbicide Magnacide (Smith *et al.*, 1995). Despite this interest, no structures of 3-hydroxypropionates appear to have been reported. We chose to prepare yttrium 3-hydroxypropionates for our entry into this area since we have used yttrium salts as the benchmark for comparison of decomposition temperatures and mechanisms in the investigations of low-temperature precursors for ceramics (Georgieva, 1995).



(1)



(2)

In poly[diaquabis(3-hydroxypropionato)yttrium(III)] bromide, (1), the two carboxylate ligands in the cation chelate to the metal *via* the hydroxyl and one of the carboxyl O atoms. Pairwise association of these units *via* coordination of the second carboxyl O atom of one of these ligands to the other metal forms dinuclear units which further associate *via* coordination of the second carboxyl O atom to adjacent metals to form sheets running parallel to (101) (Fig. 1). A similar chelating/bridging coordination mode has been found for methoxyacetate in $[Nd(O_2CCH_2OCH_3)_2(NO_3)(H_2O)]$ (Mague *et al.*, 1998). The sheets are held together by hydrogen bonding to the bromide ion. These involve the two ligand hydroxyl groups and one H atom on each of the two water molecules. In addition, the dinuclear units are reinforced by hydrogen bonds between the other H atom of each water ligand and the carboxyl O atom attached to the other metal (Fig. 1).

The chelating/bridging mode of coordination of the 3-hydroxypropionate ligand is also seen in *catena*-poly[pentaaqua(3-hydroxypropionato)yttrium(III)] bromide chloride, (2), but with only one ligand per