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# [*N*-(4-Chlorobenzoyl)-*N*′-(picolinylidene)hydrazinato]dioxovanadium(V)

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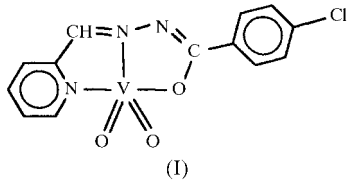
In the structure of the title compound (systematic name: {(4-chlorophenyl)[2-(2-pyridylmethylidene-$\kappa N$)hydrazono-$\kappa N^2$]methanolato-$\kappa O$}dioxovanadium(V)), $[VO_2(C_{13}H_9ClN_3O)]$, the asymmetric unit contains three independent but geometrically similar molecules. The metal centre has a distorted trigonal bipyramidal $N_2O_3$ coordination sphere. The planar monoanionic *N*,*N*,*O*-donor ligand occupies one equatorial and two axial positions, the remaining two equatorial positions being occupied by the two oxo groups.

## Comment

It is well known that vanadate acts as a potent inhibitor of phosphate-metabolizing enzymes (Rehder, 1991). During phosphate hydrolysis, it has been proposed that enzyme-bound pentavalent vanadium mimics the trigonal bipyramidal phosphorus(V) intermediate (Lindquist *et al.*, 1973; Mokry & Carrano, 1993). A pentacoordinated metal centre in *cis*-dioxovanadium(V) complexes with tridentate Schiff base ligands may have either square pyramidal or trigonal bipyramidal coordination geometry. Square pyramidal species typically dimerize by sharing oxo groups and the metal centre becomes pseudo-octahedral (Li *et al.*, 1988; Meichang *et al.*, 1988; Mokry & Carrano, 1993; Duncan *et al.*, 1997). It has been shown that by using bulky substituents on the ligand, dimerization can be prevented and trigonal bipyramidal geometry can be stabilized (Mokry & Carrano, 1993). In earlier work, we found that the reaction of bis(acetylacetonato)-oxovanadium(IV) with the *N*,*N*,*O*-donor ligand *N*-anisoyl-*N*′-(picolinylidene)hydrazine produces a dimeric pervanadyl complex in which the metal centres are hexacoordinated (Pal & Pal, 2001). However, the title mononuclear distorted trigonal bipyramidal complex, $[VO_2(pach)]$, (I), was isolated from the same vanadium starting material and *N*-(4-chlorobenzoyl)-*N*′-(picolinylidene)hydrazine (Hpach) under identical reaction conditions.




(I)

The title complex crystallizes with three independent molecules in the asymmetric unit. The structure of one of these molecules is shown in Fig. 1. The bond distances and angles for each of the three molecules are essentially identical. The $N_2O_3$ coordination sphere around the metal centre in (I) is formed by the pyridine-N, the imine-N and the amide-O donor atoms of the monoanionic planar $pach^-$ ligand and by the two oxo groups. The N—N [1.374 (5)–1.386 (5) Å], N—C [1.295 (6)–1.310 (6) Å] and C—O [1.291 (5)–1.302 (5) Å] distances in the $=N-N=C(-O^-)-$ fragments of the ligands in all three molecules are consistent with the enolate form of the amide functionality (Rath *et al.*, 1997; Sangeetha & Pal, 2000). The ligand forms two five-membered chelate rings. The chelate bite angles are very similar, all falling within the range 72.91 (16)–73.14 (16)°. In all three molecules, the V—O(oxo) distances [1.594 (4)–1.609 (3) Å] are typical for terminal oxo to vanadium(V) bonds (Sangeetha & Pal, 2000). The V—N(pyridine) [2.124 (4)–2.140 (4) Å], V—N(imine) [2.105 (4)–2.114 (4) Å] and V—O(amide) [1.963 (3)–1.972 (3) Å] bond lengths are unexceptional with respect to known vanadium(V) to pyridine-N, imine-N and deprotonated amide-O linkages (Kojima *et al.*, 1983; Rath *et al.*, 1997).

The coordination geometry around the metal centre in each of the three molecules can be best described as distorted trigonal bipyramidal. The deviations of both oxo groups from the plane formed by the coordinated pyridine-N, imine-N and amide-O donor atoms are too large to allow any plausible NNOO square plane; the maximum and minimum deviations are 1.68 and 0.86 Å, respectively. On the other hand, the maximum and minimum deviations from the mean plane formed by the metal centre, the imine-N and the two oxo

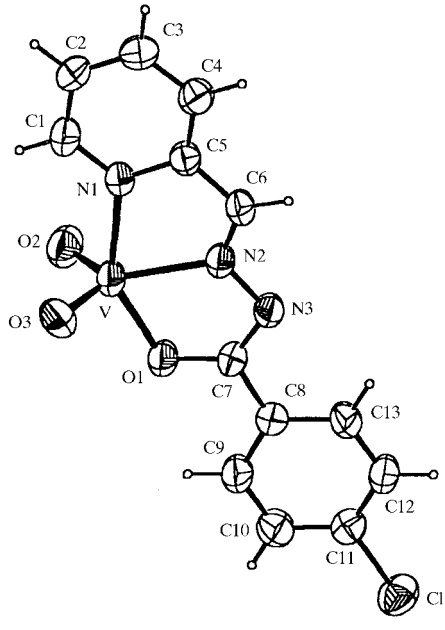



**Figure 1**
The molecular structure of one of the three independent molecules of (I) showing the atom-numbering scheme. All non-H atoms are represented by 40% probability displacement ellipsoids.

atoms are only 0.054 and 0.015 Å, respectively. Thus, the molecular structure of $[VO_2(pach)]$ approximates much more closely to trigonal bipyramidal than to square pyramidal. The tridentate ligand occupies one equatorial and two axial sites, the remaining two equatorial sites being occupied by the two oxo groups.

## Experimental

A solution of Hpach (198 mg, 0.75 mmol) in acetonitrile (20 ml) was added to a solution of $[VO(acac)_2]$ (200 mg, 0.75 mmol) in acetonitrile (20 ml) and the mixture was heated on a water bath for 15 min. The resulting dark-brown solution was concentrated by slow evaporation at room temperature. The crystalline solid which separated out was collected by filtration, washed with acetonitrile and finally dried under vacuum over anhydrous $CaCl_2$. Yield: 116 mg (45%). Analysis calculated for $C_{13}H_9ClN_3O_3V$: C 45.71, H 2.65, N 12.30%; found: C 45.67, H 2.55, N 12.14%. Selected IR bands ($cm^{-1}$): 1595 (*s*), 1493 (*s*), 1449 (*s*), 1391 (*s*), 1343 (*m*), 1296 (*w*), 1263 (*w*), 1219 (*w*), 1173 (*m*), 1146 (*m*), 1071 (*s*), 1013 (*w*), 949 (*s*), 916 (*m*), 845 (*m*), 775 (*w*), 745 (*s*), 677 (*w*), 648 (*w*). Electronic spectral data in $CH_2Cl_2$ [nm ($dm^3\ mol^{-1}\ cm^{-1}$)]: 402 (19 500), 292 (13 600), 237 (14 500).

*Crystal data*

$[VO_2(C_{13}H_9ClN_3O)]$
$M_r$ = 341.62
Monoclinic, $P2_1/n$
$a$ = 7.1139 (9) Å
$b$ = 39.501 (5) Å
$c$ = 14.7094 (13) Å
$\beta$ = 96.636 (9)°
$V$ = 4105.7 (8) Å$^3$
$Z$ = 12
$D_x$ = 1.658 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 9.5–12.4°
$\mu$ = 0.932 mm$^{-1}$
$T$ = 298 K
Block, brown
0.40 × 0.36 × 0.32 mm

*Data collection*

Enraf–Nonius MACH3 four-circle diffractometer
Profile data from $\omega$ scans
Absorption correction: empirical based on $\psi$ scan (*DATCOR*; Reibenspies, 1989)
$T_{min}$ = 0.884, $T_{max}$ = 0.990
7956 measured reflections
7219 independent reflections
3565 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018
$\theta_{max}$ = 24.97°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 46$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity decay: none

*Refinement*

Refinement on $F^2$
$R$ = 0.049
$wR$ = 0.126
$S$ = 1.013
7219 reflections
568 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 1.7700P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.39 e Å$^{-3}$

H atoms were placed geometrically and refined using a riding model, with C—H distances constrained to 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *Xtal*3.4 (Hall *et al.*, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX*6*a* (McArdle, 1995); software used to prepare material for publication: *SHELXL*97.

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

| | | | |
|---|---|---|---|
| V—N1 | 2.140 (4) | V*A*—O2*A* | 1.609 (3) |
| V—N2 | 2.114 (4) | V*A*—O3*A* | 1.594 (4) |
| V—O1 | 1.972 (3) | V*B*—N1*B* | 2.139 (4) |
| V—O2 | 1.607 (4) | V*B*—N2*B* | 2.112 (4) |
| V—O3 | 1.605 (4) | V*B*—O1*B* | 1.963 (3) |
| V*A*—N1*A* | 2.124 (4) | V*B*—O2*B* | 1.608 (4) |
| V*A*—N2*A* | 2.105 (4) | V*B*—O3*B* | 1.605 (4) |
| V*A*—O1*A* | 1.965 (3) | | |
| N1—V—N2 | 72.98 (15) | N2*A*—V*A*—O2*A* | 129.02 (19) |
| N1—V—O1 | 145.87 (16) | N2*A*—V*A*—O3*A* | 121.95 (19) |
| N1—V—O2 | 96.01 (18) | O1*A*—V*A*—O2*A* | 103.08 (16) |
| N1—V—O3 | 96.42 (18) | O1*A*—V*A*—O3*A* | 103.41 (18) |
| N2—V—O1 | 72.95 (15) | O2*A*—V*A*—O3*A* | 108.6 (2) |
| N2—V—O2 | 127.05 (19) | N1*B*—V*B*—N2*B* | 73.14 (16) |
| N2—V—O3 | 123.80 (19) | N1*B*—V*B*—O1*B* | 145.25 (16) |
| O1—V—O2 | 102.73 (17) | N1*B*—V*B*—O2*B* | 94.94 (18) |
| O1—V—O3 | 104.08 (17) | N1*B*—V*B*—O3*B* | 98.36 (18) |
| O2—V—O3 | 108.6 (2) | N2*B*—V*B*—O1*B* | 73.04 (15) |
| N1*A*—V*A*—N2*A* | 72.91 (16) | N2*B*—V*B*—O2*B* | 133.62 (18) |
| N1*A*—V*A*—O1*A* | 145.89 (16) | N2*B*—V*B*—O3*B* | 117.16 (19) |
| N1*A*—V*A*—O2*A* | 96.34 (18) | O1*B*—V*B*—O2*B* | 102.54 (18) |
| N1*A*—V*A*—O3*A* | 96.46 (18) | O1*B*—V*B*—O3*B* | 103.94 (18) |
| N2*A*—V*A*—O1*A* | 73.06 (15) | O2*B*—V*B*—O3*B* | 108.8 (2) |

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1436). Services for accessing these data are described at the back of the journal.

## References

Duncan, C. A., Copeland, E. P., Kahwa, I. A., Quick, A. & Williams, D. J. (1997). *J. Chem. Soc. Dalton Trans.* pp. 917–919.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). Editors. *Xtal*3.4 *User's Manual.* University of Western Australia, Australia.
Kojima, A., Okazaki, K., Ooi, S. & Saito, K. (1983). *Inorg. Chem.* **22**, 1168–1174.
Li, X., Lah, M. S. & Pecoraro, V. L. (1988). *Inorg. Chem.* **27**, 4657–4664.
Lindquist, R. N., Lynn, J. L. Jr & Lienhard, G. E. (1973). *J. Am. Chem. Soc.* **95**, 8762–8768.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
Meichang, S., Xun, D. & Yougi, Y. (1988). *Sci. Sin. Ser. B* (*Engl. Ed.*), **31**, 789–799.
Mokry, L. M. & Carrano, C. J. (1993). *Inorg. Chem.* **32**, 6119–6121.
Pal, S. N. & Pal, S. (2001). *J. Chem. Crystallogr.* In the press.
Rath, S. P., Mondal, S. & Chakravorty, A. (1997). *Inorg. Chim. Acta*, **263**, 247–253.
Rehder, D. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 148–167.
Reibenspies, J. (1989). *Q&D Crystallographic Program Package*. Texas A & M University, College Station, Texas, USA.
Sangeetha, N. R. & Pal, S. (2000). *Bull. Chem. Soc. Jpn*, **73**, 357–363.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.