average length of 2.326 Å, and bonded to five water O atoms with an average Er—O(water) bond length of 2.366 Å. The coordination number of the Er ion is eight and its coordination polyhedron can be described as a distorted triangular dodecahedron. In the crystal, the proline amino groups remain protonated and unbonded to the metal ions, but are associated with O atoms of the same proline to form intraligand hydrogen bonds [N(1)···O(7) 2.684 Å, N(2)···O(6) 2.627 Å]. The distances between Cl anions and Er cations are longer than 4.639 Å and the average of the shortest distances between Cl anions and N atoms of the amino groups is 3.165 Å, indicating that the Cl anions do not coordinate with the Er cations but are attracted electrostatically to the amino groups.

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Structure of Dipotassium (Nitrilo-κN-triacetato-κ³O,O'',O'''')oxoperoxovanadate(V)–Water (1/2)

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Abstract. $K_2[V(C_6H_6NO_6)O(O_2)].2H_2O$, $M_r = 401.28$, orthorhombic, $Pnam$, $a = 7.597\,(5)$, $b = 12.951\,(3)$, $c = 13.131\,(5)$ Å, $V = 1291.9\,(1)$ Å^3, $Z = 4$, $D_x = 2.06$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 14.4$ cm^{-1}, $F(000) = 808$, $T = 295$ K, $R = 0.019$ for 1820 unique reflections. Vanadium is surrounded by a seven-membered coordinating pentagonal bipyramid formed by a tetradentate nitrilotriacetate ligand, a bidentate peroxo group and a vanadyl oxygen. The bipyramid is symmetrical relative to the mirror plane passing through the V atom, the apical O atoms, the equatorial N atom and the midpoint between the peroxo O atoms. The nitrilotriacetate ligand forms three glycinate rings with the V atom, one of which coincides with the mirror plane, the two others being symmetrical relative to the plane. The compound is remarkably stable towards decomposition.

Introduction. This work continues our structural study of peroxovanadates (Lapshin, Smolin, Shepelev, Gyepesova & Schwendt, 1989; Lapshin, Smolin, Shepelev, Schwendt & Gyepesova, 1990a,b), in which all peroxovanadates were unstable. This has been noted by other authors (Stomberg, 1984a; Volnov, 1987). The interesting feature of the present compound is its long-term stability in air at room temperature. Since peroxo complexes are thermodynamically unstable it is important to study the stabilizing effect of certain ligands and to correlate this with the structure.

Experimental. A single red crystal with approximate dimensions $0.40 \times 0.45 \times 0.50$ mm was mounted on an automatic three-circle normal-beam single-crystal X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation; ω–2θ scan method. Lattice parameters were determined from the setting of 22 reflec-

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tions with $11 \le \theta \le 45°$. Only unique reflections in one octant of reciprocal space ($2\theta \le 99°$, $0 \le h \le 15$, $0 \le k \le 26$, $0 \le l \le 13$) were measured. 2072 reflections were obtained with the modified Oatley & French (1982) profile analysis procedure. One control reflection, monitored every 30 reflections, showed no significant variation in intensity. 1820 observed reflections having $I \ge 4\sigma(I)$ were used in the subsequent analysis. Data were corrected for Lorentz and polarization effects. Absorption was ignored.

Coordinates of the V atom were determined from the Patterson function, remaining non-H atoms were located in subsequent ρ maps while all H atoms were located in $\Delta\rho$ maps. Structure was refined by blocked full-matrix least squares on F using $ORFLS$ (Busing, Martin & Levy, 1962); $\Sigma w(|F_o| - |F_c|)^2$ was minimized with the Cruickshank (1965) weighting scheme: $w = (2|F_o|_{min} + |F_o| + 2F_o^2/|F_o|_{max})^{-1}$. All non-H atoms were refined anisotropically. The isotropic displacement parameter of each H atom was taken to be equal to the equivalent isotropic displacement parameter B_{eq} of the parent atom and not refined.

Final discrepancy indices were $R = 0.019$, $wR = 0.024$ for 1820 observed reflections; $(\Delta/\sigma)_{max} = 0.04$, $S = 1.158$ for 134 variables. The max. and min. peak heights in the final $\Delta\rho$ map were 0.34 and -0.30 e Å^{-3}, respectively. Computer programs used include the $AREN$ system of programs (Andrianov, 1987) and $ORTEP$II (Johnson, 1976). All calculations were performed on an IBM PC/AT 386 computer. Scattering factors for neutral atoms were taken from Hanson, Herman, Lea & Skillman (1964). Table 1* lists the final atomic parameters. The main interatomic distances and bond angles for the title compound are given in Table 2. A projection of the atomic arrangement on the yz plane is given in Fig. 1. The vanadium complex together with the atom-labelling scheme is shown in Fig. 2.

Discussion. The structure described here consists of the peroxo complex $[VO(O_2)nta]^{2-}$ (where nta is the nitrilotriacetate ligand), K^+ ions and water molecules. They are held together by electrostatic and hydrogen-bonding forces. The vanadium–peroxo complex exhibits a pentagonal-bipyramidal polyhedron that is symmetrical relative to the mirror plane passing through the V atom, the apical O(1) and O(5) atoms, the equatorial N atom and the midpoint

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, hydrogen-bond geometry and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55768 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1026]

Table 1. *Positional parameters and equivalent isotropic displacement factors with e.s.d.'s in parentheses for non-H atoms*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
V	0.30607 (3)	0.47669 (1)	0.25	1.10 (1)
K	0.36603 (3)	0.26941 (2)	0.60243 (2)	1.99 (1)
O(1)	0.3812 (2)	0.3604 (1)	0.25	2.53 (3)
O(2)	0.4901 (1)	0.5541 (1)	0.3044 (1)	2.39 (2)
O(3)	0.2392 (1)	0.4713 (1)	0.4004 (1)	1.95 (2)
O(4)	0.0946 (1)	0.3815 (1)	0.5187 (1)	2.27 (2)
O(5)	0.1470 (1)	0.6106 (1)	0.25	1.70 (3)
O(6)	−0.1188 (2)	0.6800 (1)	0.25	1.72 (3)
O(7)	0.3834 (2)	0.6259 (1)	0.5271 (1)	3.04 (3)
N	0.0366 (2)	0.4140 (1)	0.25	1.16 (2)
C(1)	0.1228 (1)	0.4048 (1)	0.4295 (1)	1.56 (2)
C(2)	0.0246 (2)	0.3513 (1)	0.3436 (1)	1.70 (2)
C(3)	−0.0198 (2)	0.6040 (1)	0.25	1.21 (3)
C(4)	−0.0974 (2)	0.4973 (1)	0.25	1.74 (3)

Table 2. *Bond distances (Å), interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

Vanadium coordination

V—O(1)	1.610 (1)	V—O(5)	2.113 (1)
V—O(2)	1.862 (1) 2 ×	V—N	2.202 (1)
V—O(3)	2.040 (1) 2 ×	O(2)—O(2^i)	1.428 (1)

O(1)—V—O(2)	103.73 (4) 2 ×	O(2)—V—O(5)	89.28 (4) 2 ×
O(1)—V—O(3)	93.22 (6) 2 ×	O(2)—V—N	153.6 (1) 2 ×
O(1)—V—O(5)	165.87 (3)	O(3)—V—O(3^i)	150.89 (2)
O(1)—V—N	89.10 (2)	O(3)—V—O(5)	83.42 (4) 2 ×
O(2)—V—O(2^i)	45.07 (4)	O(3)—V—N	75.84 (4) 2 ×
O(2)—V—O(3)	80.48 (6) 2 ×	O(5)—V—N	76.77 (1)
O(2)—V—O(3^i)	125.21 (6) 2 ×		

Nitrilotriacetate ligand

C(1)—O(3)	1.291 (1)	C(1)—C(2)	1.519 (1)
C(1)—O(4)	1.228 (1)	C(3)—C(4)	1.501 (2)
C(3)—O(5)	1.269 (1)	N—C(2)	1.475 (1) 2 ×
C(3)—O(6)	1.238 (1)	N—C(4)	1.484 (1)

O(3)—C(1)—O(4)	124.4 (1)	O(6)—C(3)—C(4)	119.49 (6)
O(3)—C(1)—C(2)	114.8 (1)	C(1)—C(2)—N	109.7 (1)
O(4)—C(1)—C(2)	120.6 (1)	C(3)—C(4)—N	113.55 (6)
O(5)—C(3)—O(6)	123.53 (3)	C(2)—N—C(2^i)	112.80 (7)
O(5)—C(3)—C(4)	117.01 (4)	C(2)—N—C(4)	110.9 (1)

Potassium

K···O(4)	2.750 (1)	K···O(4^v)	2.836 (1)
K···O(6^{iii})	2.777 (1)	K···O(7^{ii})	2.890 (1)
K···O(2^{ii})	2.813 (1)	K···O(6^{iv})	2.964 (1)
K···O(5^{iv})	2.828 (1)	K···O(7^{vi})	3.152 (1)

Symmetry code: (i) x, y, $\frac{1}{2} - z$; (ii) $1 - x$, $1 - y$, $1 - z$; (iii) $-x$, $1 - y$, $\frac{1}{2} + z$; (iv) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} + z$; (v) $\frac{1}{2} + x$, $\frac{1}{2} - y$, z; (vi) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $1 - z$.

between the peroxo O(2) and O(2^i) atoms (the labelling is according to Table 2) and perpendicular to the z axis. The equatorial plane of the bipyramid passes through the N, O(2) and O(2^i) atoms and also through the symmetrical carboxylate O(3) and O(3^i) atoms from nta [max. deviation from planarity is 0.037 (2) Å]. The V atom lies 0.211 (2) Å above the equatorial plane towards the vanadyl O(1) atom. The V=O(1) bond length of 1.610 (1) Å indicates it is a double bond. The bond length from V to the carb-

oxylate O(5) atom of nta, 2.113 (1) Å, is long compared with the other vanadium–carboxylate oxygen bonds [2.040 (1) Å]. This lengthening agrees well with the general observation that for pentagonal-bipyramidal oxoperoxometallates, the M—L(apical) bond *trans* to the M=O bond is longer than the M—L(equatorial) bond (Stomberg, 1984b, 1988). The difference between the V—N and V—O(equatorial) distances is more than the difference in the covalent radii of nitrogen and oxygen, ~ 0.04 Å (Pauling, 1960). This may be explained by the fact that the N atom is *trans* to the peroxo group; the N—V—O(peroxo) angle being 153.6 (1)°.

Two V—O(peroxo) bonds [1.862 (1) Å] are symmetrical relative to the mirror plane. The O—O

peroxo bond length of 1.428 (1) Å agrees closely with the bond lengths found in other monoperoxovanadates (Szentivanyi & Stomberg, 1983; Stomberg, 1986).

The tetradentate nitrilotriacetate ligand forms three glycinate rings with the V atom. One of these rings, consisting of V, O(5), C(3), C(4) and N, is strictly planar, because the atoms of the ring are situated in the mirror plane. The two other rings, consisting of V, O(3), C(1), C(2) and N and V, O(3^i), C(1^i), C(2^i) and N, are symmetrically equivalent to each other in relation to the mirror plane and almost planar [max. deviation from planarity is 0.280 (2) Å]. The first ring forms a dihedral angle of ± 85.79 (2)° with the other and 90° with the equatorial plane of the bipyramid. The quasi-planar rings form angles of 171.58 (2)° with each other and ± 7.39 (2)° with the equatorial plane.

The N—C, C—C and C—H distances are as expected. The C—O bond lengths within the carboxylate groups vary according to whether the O atoms are coordinated to the metal atom or not; C—O$_c$ 1.269 (1), 1.291 (1) Å and C—O$_u$ 1.228 (1), 1.238 (1) Å.

The water molecule is weakly hydrogen bonded to the equatorial carboxylate O atoms of neighbouring complexes; the O···O contacts are 2.825 (1) and 3.273 (1) Å. As can be seen in Fig. 1, where hydrogen bonds are shown by dotted lines, the peroxo complexes, connected by water molecules, form folded chains extended along the z axis.

The K ions occupy positions between such chains and, owing to their own contacts with the surrounding O atoms of different complexes and water molecules, link the entire structure in a three-dimensional network. The coordination geometry about the K atom may be described as a disordered square antiprism. The individual K—O distances less than the sum of the van der Waals radii (3.2 Å) of K and O are listed in Table 2.
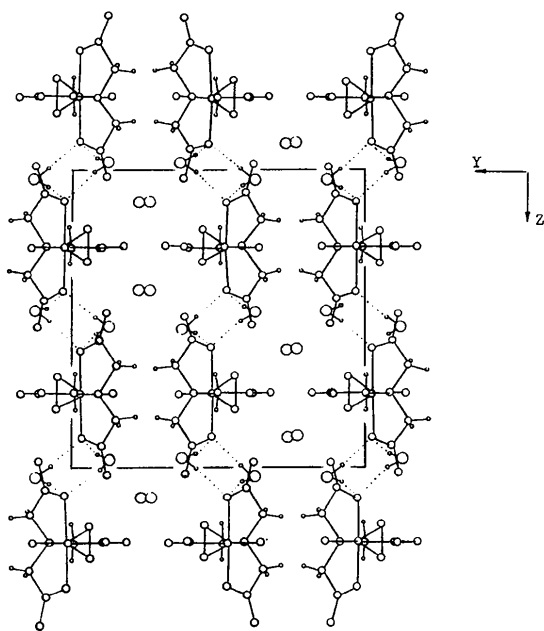

Fig. 1. Packing diagram viewed along the *x* axis showing hydrogen bonding involving water molecules giving folded chains elongated along the *z* axis. Hydrogen bonds are represented by dotted lines.
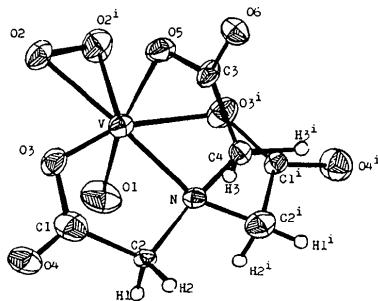

Fig. 2. *ORTEP* diagram of the title compound showing the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and H atoms are drawn with arbitrary radii.

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Structure of Bis{2'-[α-(2-pyridyl)benzylidene]salicylohydrazido}zinc(II)

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Abstract. [Zn(C₁₉H₁₄N₃O₂)₂], $M_r = 698.06$, mono-
clinic, $P2_1/c$, $a = 13.460$ (5), $b = 9.632$ (3), $c =$
24.667 (2) Å, $\beta = 107.79$ (6)°, $V = 3045$ (2) Å³, $Z =$
4, $D_m = 1.54$ (by flotation in xylene/chloroform), D_x
$= 1.523$ Mg m⁻³, λ(Mo $K\alpha$) = 0.71069 Å, $\mu =$
0.877 mm⁻¹, $F(000) = 1440$, $T = 294$ K, final $R =$
0.039, $wR = 0.039$ for 3626 observed diffractometer
data. The two non-planar tridentate C₁₉H₁₄N₃O₂
ligands interact differently with the Zn atom. They
are stabilized by intramolecular O—H···N hydrogen
bonds. The Zn atom has a distorted octahedral
environment consisting of two pyridine (py) N atoms
[Zn—N(py) = 2.044 (4), 2.206 (4) Å], two azo N
atoms [Zn—N(azo) = 2.046 (3), 2.078 (3) Å], a car-
bonyl (keto) O atom and an enolate O⁻ atom
[Zn—O = 2.070 (4), 1.947 (3) Å]. The two N(py)
atoms are *cis* [N(3)—Zn—N(4) = 86.9 (2)°] while the
N(azo) atoms are *trans* [N(2)—Zn—N(5) =
164.9 (1)°].

Introduction. Several complexes of the tridentate
ligand 2'-[α-(2-pyridyl)benzylidene]salicylohydrazide
(pbsH) with transition and non-transition elements
and also with lanthanides (Dutta & Hossain, 1984;
Dutta & Das, 1984) have been synthesized. The
neutral ligand pbsH may exist in tautomeric keto
and enol forms. The present work was carried out to
determine whether the structural features of the title
compound are similar to those in the Ni and Sm
complexes (Seth & Chakraborty, 1984; Dan, Seth &
Chakraborty, 1989) and to discover the nature of the

Zn—N bonding, the planarity of the ligand and the
bonding within the molecule.

(A)   (B)
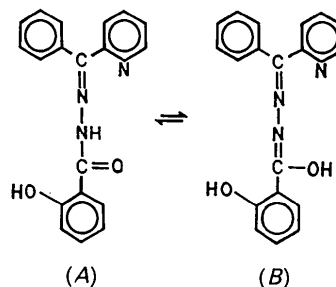
Experimental. The title compound was synthesized
by refluxing an aqueous solution of zinc acetate with
an ethanolic solution of the Schiff-base ligand
pbsH. Thin plate-shaped yellow crystals were
obtained by slow evaporation of a solution in a
mixture of acetone and alcohol at room temperature.
Approximate lattice constants from rotation and
Weissenberg photographs, accurate values by least-
squares treatment of 25 randomly chosen reflections
with $10.2 < \theta < 13.5°$, Enraf–Nonius CAD-4 diffrac-
tometer, graphite-monochromated Mo $K\alpha$ radiation,
crystal *ca* 0.30 × 0.37 × 0.42 mm; intensity data for
$4.6 \le 2\theta \le 55.0°$, index range $-15 \le h \le 15$, $0 \le k \le$
12, $0 \le l \le 29$, ω–2θ scans; three standard reflections
monitored periodically did not vary significantly
during data collection; 5896 independent reflections
were recorded, 3626 $[I \ge 3\sigma(I)]$ employed for the
structure determination. Lorentz–polarization cor-
rection but no absorption correction. The approxi-