sandwiching of the perovskite layers between the organic cations is shown in Fig. 2. The plane of the phenyl ring in the cation is rotated approximately 90° to the plane of its aliphatic tail. Interdigitation of the phenyl groups between layers is not observed, in accord with the very delicate nature of the crystals.

The structural characteristics of the copper(II) halide layer perovskites have recently been reviewed (Willett, Place & Middleton, 1989). The non-conventional choice of the *Pcab* space group allows direct comparison with that summary. The $PhC_2H_4NH_3^+$ salts reported here are isostructural with $(EtNH_3)_2CuCl_4$ (Steadman & Willet, 1970) and $(PrNH_3)_2CuCl_4$ (Barendregt & Schenk, 1970). The stacking of layers is of the staggered arrangement, with copper ions located at the corners and face centers of the unit cell. The *Pcab* space group is derived from the parent *I4/mmm* structure of the undistorted tetragonal layer perovskites (Heger, Mullen & Knorr, 1975) *via* a descent of symmetry involving (1) the loss of the fourfold axis, (2) a rotation of the in-layer axes by 45°, doubling the unit-cell volume, and (3) a loss of the mirror operation in the plane of the layer. The layer group is $P2_1/a$, where the *a*-glide operation generates the pleated nature of the structure parallel to the *a* axis.

The Cu—*X* distances compare very favorably with those of the other salts in the layer perovskite series, where the Cu—Cl and Cu—Br distances average 2·291 and 2·439 Å, respectively. The semi-coordinate distances are among the shortest reported. It is expected theoretically, and demonstrated experimentally, that the value of the ferromagnetic interlayer coupling, *J*, should increase monotonically as the semi-coordinate Cu···*X* distances decrease (Willett *et al.*, 1989). The value of $J/k = 19{\cdot}0$ K for the chloride salts for a Cu···Cl distance of 2·899 Å is in accord with several other salts where $J/k = 19{\cdot}0 \pm 0{\cdot}4$ K for Cu···Cl values of $2{\cdot}90 \pm 0{\cdot}03$ Å. The only bromide salt with a similarly short semi-coordinate distance is $(NH_3C_2H_4NH_3)CuBr_4$ (Cu···Br = 3·034 Å), where $J/k = 38{\cdot}2$ K.

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Dichlorobis(*N*,*N*-dimethylacetamide)oxovanadium(IV)

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Abstract. $[VCl_2O(C_4H_9NO)_2]$, $M_r = 312{\cdot}09$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}635$ (2), $b = 12{\cdot}237$ (2), $c = 13{\cdot}683$ (2) Å, $V = 1445{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}43$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 9{\cdot}80$ cm^{-1}, $F(000) = 644$, $T = 295$ K, $R = 0{\cdot}043$ for 1409 unique observed reflections [$F_o > 4\sigma(F_o)$]. The compound has a trigonal bipyramidal structure with the two chloro ligands and the vanadyl oxygen in the trigonal plane and the O atoms of the acetamide groups near the axis with O—V—O = 156·6°.

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Introduction. Vanadium in its oxidation states IV and V has a versatile coordination geometry, commonly encompassing tetrahedral (coordination number CN = 4), tetragonal pyramidal (CN = 5), octahedral and trigonal prismatic (CN = 6), and pentagonal bipyramidal (CN = 7) arrangements. The trigonal bipyramidal case for CN = 5 is rare, an example being the cyclothiazeno complex $[(S_2N_3)VCl_2(NC_5H_5)]$ investigated by Christophersen, Klingelhöfer, Müller, Dehnicke & Rehder (1985). Further, as has been shown by a neutron diffraction study (Wlodawer, Miller & Sjölin, 1983), vanadium in the ternary complex formed between vanadate(V), uridine and ribonuclease *A* is at the centre of a trigonal bipyramid. This observation is of some importance in the context of a trigonal transition state for the analogous phosphorus compound postulated for the reaction path of the enzymatic cleavage of the phosphodiester bond in RNA (Heinemann & Saenger, 1983). Vanadium can thus be considered to mimic the otherwise unavailable phosphorus intermediate in RNA hydrolysis. A trigonal-bipyramidal complex has also been postulated, on the basis of a ^{51}V NMR analysis, for weak complexes formed between vanadate and diols (Gresser & Tracey, 1986) or vanadate and lactate in aqueous solution (Tracey, Gresser & Parkinson, 1987). In our endeavour to build appropriate model compounds, we have now prepared and crystallized a neutral V^{IV} species, carrying the bio-related acetamide ligands in the axial positions of an overall trigonal bipyramidal arrangement.

Experimental. The title compound was prepared by reacting 11·26 g (0·129 mol) *N,N*-dimethylacetamide, dissolved in 40 ml of dry pentane and cooled to 77 K, with a solution of 5·6 g (0·032 mol) $VOCl_3$ in 30 ml of pentane (the $VOCl_3$ was added within 20 min, and the mixture was stirred vigorously during the addition). The reaction mixture was then slowly warmed to room temperature and refluxed for 10 min. After evaporation of the solvent, a red-brown solid was obtained with the ^{51}V NMR characteristics (pentane, $\delta = -362$ relative to $VOCl_3$) of a vanadium(V) complex of composition $VOCl(O)_2$ or $[VOCl_2(O)_2]^-$ (Weidemann & Rehder, 1986). This compound was dissolved in dry and purified tetrahydrofuran (THF) to give a turquoise solution. Removal of the THF resulted, after several washings with small amounts of ethanol, in a blue residue of the V^{IV} acetamide complex [ν(V=O) = 996 cm^{-1}].

Blue crystals were grown by adding pentane to a solution of the blue product in ethanol. A crystal of approximate dimensions 0·4 × 0·4 × 0·5 mm was used for data collection on a Syntex $P2_1$ diffractometer (graphite monochromator, Mo $K\alpha$ radiation) at room temperature. Cell constants were determined from 20 reflections (2θ = 10–25°). Space-group ($P2_12_12_1$) determination was carried out on the basis of no conditions for reflections *hkl*, 0*kl*, *h*0*l* and *hk*0, and the systematic extinctions of the reflections with *h*00, $h \neq 2n$, 0*k*0, $k \neq 2n$, and 00*l*, $l \neq 2n$. For the structure determination, 5832 reflections were collected (θ–2θ scan mode, 2θ range 4·5–55°). Three standard reflections ($0\bar{3}5$, $2\bar{1}1$, $\bar{3}30$) were used. 1409 reflections with $F_o > 4\sigma(F_o)$ were used in the subsequent structure solution and refinement. Correction for absorption has not been carried out. Range of *h*, *k* and *l*: *h*(0→11), *k*(0→15), *l*(0→17); $(\sin\theta)/\lambda \leq$ 0·6497 Å^{-1}. The structure was solved by Patterson methods using the *SHELXS*86 program system (Sheldrick, 1986). H atoms were refined as rotors riding on the pivot C atoms with a common isotropic thermal factor for all H atoms. For refinements (164 parameters), the program *SHELX*76 (Sheldrick,

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters for the non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	*y*	*z*	U_{eq}(Å^2)
V	0·6404 (1)	1·0206 (1)	0·1114 (1)	0·050 (1)
Cl(1)	0·7382 (2)	0·8448 (1)	0·1076 (2)	0·071 (1)
Cl(2)	0·3998 (2)	1·1032 (1)	0·1130 (2)	0·072 (2)
O	0·7737 (4)	1·1087 (3)	0·1133 (4)	0·068 (4)
O(11)	0·6091 (6)	0·9993 (3)	−0·0326 (3)	0·068 (5)
N(11)	0·4731 (6)	1·0134 (5)	−0·1695 (4)	0·065 (5)
C(11)	0·5571 (7)	1·0583 (5)	−0·1005 (4)	0·054 (5)
C(12)	0·5998 (9)	1·1774 (5)	−0·1061 (6)	0·078 (7)
C(13)	0·4429 (10)	0·8965 (6)	−0·1679 (7)	0·095 (10)
C(14)	0·4168 (10)	1·0736 (9)	−0·2543 (5)	0·102 (11)
O(21)	0·6100 (6)	0·9919 (4)	0·2535 (3)	0·074 (5)
N(21)	0·4776 (6)	1·0024 (4)	0·3929 (4)	0·064 (5)
C(21)	0·5626 (8)	1·0489 (6)	0·3250 (4)	0·062 (7)
C(22)	0·6073 (10)	1·1664 (6)	0·3338 (5)	0·077 (8)
C(23)	0·4192 (9)	1·0593 (8)	0·4788 (5)	0·085 (9)
C(24)	0·4491 (10)	0·8836 (6)	0·3888 (7)	0·095 (9)

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and planes* (*deviations of atoms from plane in* Å)

Distances and bond angles for the second dimethylacetamide ligand (atoms labelled 2*i*) are omitted since they are identical to those for the atoms labelled 1*i* within the limits of error

V—O	1·577 (4)	Cl(1)—V—Cl(2)	137·4 (1)
V—Cl(1)	2·311 (2)	O—V—Cl(1)	111·7 (2)
V—Cl(2)	2·311 (2)	O—V—Cl(2)	110·9 (2)
V—O(11)	2·007 (4)	O(11)—V—O(21)	156·6 (2)
V—O(21)	1·993 (4)	N(11)—C(11)—O(11)	119·3 (6)
C(11)—O(11)	1·259 (7)	N(11)—C(11)—C(12)	120·2 (6)
C(11)—C(12)	1·506 (8)	C(11)—N(11)—C(13)	120·0 (6)
C(11)—N(11)	1·311 (8)	C(11)—N(11)—C(14)	123·2 (6)
N(11)—C(13)	1·457 (10)	C(13)—N(11)—C(14)	116·7 (6)
N(11)—C(14)	1·454 (10)	C(11)—O(11)—V	134·3 (4)

Plane 1: V (0·0), Cl(1) (0·0), Cl(2) (0·0), O (0·002)
Plane 2: C(11) (−0·013), C(12) (0·029), N(11) (−0·023), C(13) (0·049), C(14) (0·008)
Plane 3: N(11) (−0·021), C(11) (0·010), C(13) (0·019), C(14) (0·017)
Plane 4: N(11) (0·006), C(11) (−0·022), C(12) (0·011), O(11) (0·005)

1976) was used. Final $R = 0{\cdot}042$, $wR = 0{\cdot}043$, $w = 1{\cdot}3264/[\sigma^2(F_o) + 0{\cdot}0005F^2]$, $\Delta/\sigma \leq 0{\cdot}1$. Max. and min. heights in final difference Fourier synthesis were 0·34 and $-0{\cdot}23$ e Å^{-3}, respectively. No secondary-extinction effects were detected. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974), *f'* and *f''* values from Cromer & Liberman (1970).

Discussion. Atomic coordinates and U_{eq} values are listed in Table 1,* selected bond lengths, bond angles and planes in Table 2. The molecular structure of $[VCl_2O(C_4H_9NO)]$, together with the labelling scheme, is depicted in Fig. 1, and the crystal packing in Fig. 2.

The coordination environment of vanadium is trigonal bipyramidal with Cl(1), Cl(2), V and O on the plane (plane 1) and the O atoms of the acetamide ligand on the axis. The trigonal plane is a mirror plane for the molecule. The angle O(11)—V—O(12) (156·6°) deviates significantly from the ideal arrangement of a trigonal bipyramid. The V—O single and double bond lengths are 'normal'. V—Cl bond lengths (2·31 Å) are similar to those of other chloro–oxovanadium complexes such as tetragonal $[VOCl_4]^-$ (2·26 Å; Beindorf, Strähle, Liebelt & Dehnicke, 1980) and $[VCl_2O(OPPh_3)_2]$ (2·30 Å; Caira & Gellatly, 1980), and octahedral $[\{VCl_2O(H_2O)\}_2(\mu\text{-}Cl)_2]^{2-}$ (2·37 Å; Priebsch, Weidemann, Rehder & Kopf, 1986). C—O bond lengths (1·26 Å) and the distances between the carbamide carbons [C(11), C(21)] and nitrogen (1·31 Å) indicate that there is considerable delocalization of the electron density throughout the ligand, a view which is backed up by the nearly planar arrangement not only around C(11) and N(11) (planes 3 and 4) but also in the ligand backbone (plane 2).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52408 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

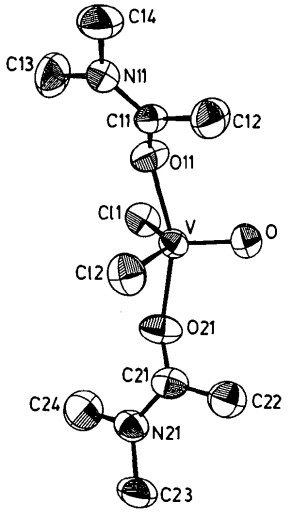

Fig. 1. Molecular structure with atomic labelling scheme. The harmonic parts of the displacement ellipsoids are drawn at the 50% probability level.

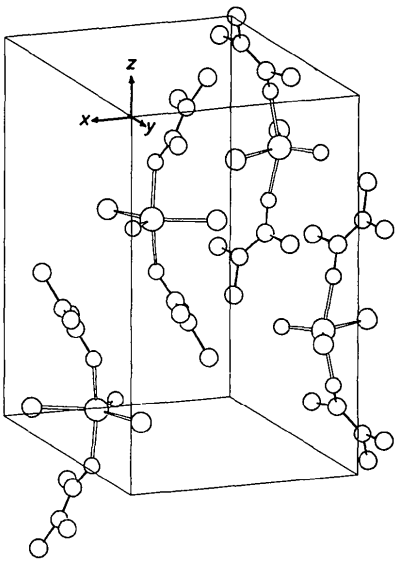

Fig. 2. Unit-cell packing diagram.

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