

**Data collection**

Enraf–Nonius CAD-4 diffractometer  
 2 $\theta$ / $\omega$  scans  
 Absorption correction:  $\psi$  scans (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.493$ ,  $T_{\max} = 0.528$   
 4319 measured reflections  
 3993 independent reflections

3993 reflections with  $F > 0$   
 $R_{\text{int}} = 0.019$   
 $\theta_{\max} = 22.5^\circ$   
 $h = 0 \rightarrow 16$   
 $k = 0 \rightarrow 13$   
 $l = -18 \rightarrow 18$   
 3 standard reflections  
 frequency: 167 min  
 intensity decay: none

**Refinement**

Refinement on  $F$   
 $R = 0.024$   
 $wR = 0.022$   
 $S = 2.90$   
 3993 reflections  
 417 parameters  
 H atoms: see below  
 Weighting scheme based on measured e.s.d.'s  
 $(\Delta/\sigma)_{\max} = 0.034$

$\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: Larson (1970)  
 Extinction coefficient: 103 (2)  
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Mo1—O1	2.352 (3)	Mo4—O16	1.707 (3)
Mo1—O2	1.937 (3)	Mo4—O17	1.708 (3)
Mo1—O3	2.307 (3)	Mo4—O18	2.224 (3)
Mo1—O4	1.905 (3)	Mo4—O19	1.950 (3)
Mo1—O5	1.703 (3)	Mo5—O1	2.347 (3)
Mo1—O6	1.708 (3)	Mo5—O2	1.943 (3)
Mo2—O3	2.405 (3)	Mo5—O15	2.197 (3)
Mo2—O4	1.903 (3)	Mo5—O19	1.937 (3)
Mo2—O7	2.211 (3)	Mo5—O20	1.706 (3)
Mo2—O8	1.973 (3)	Mo5—O21	1.701 (3)
Mo2—O9	1.698 (3)	P1—O3	1.535 (3)
Mo2—O10	1.708 (3)	P1—O11	1.509 (3)
Mo3—O7	2.367 (3)	P1—O15	1.556 (3)
Mo3—O8	1.933 (3)	P1—C1	1.799 (4)
Mo3—O11	2.223 (3)	P2—O1	1.544 (3)
Mo3—O12	1.910 (3)	P2—O7	1.549 (3)
Mo3—O13	1.703 (3)	P2—O18	1.508 (3)
Mo3—O14	1.725 (3)	P2—C3	1.786 (4)
Mo4—O12	1.907 (3)	C1—C2	1.519 (6)
Mo4—O15	2.376 (3)	C3—C4	1.521 (6)

H atoms were located geometrically (N—H and C—H = 0.95  $\text{\AA}$ ) and from difference maps for the O31 atom. The H atoms of the O32 water molecule were not located.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *RC85* (Baird, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996). Molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996). Software used to prepare material for publication: *CRYSTALS*.

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: TA1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

*Acta Cryst.* (1997), **C53**, 202–204

**Dichloro( $\eta^5$ -cyclopentadienyl)(phenylimido)vanadium(V)**

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**Abstract**

The title compound, [VCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>N)], contains vanadium in a tetrahedral coordination geometry, with the cyclopentadienyl (Cp) ligand occupying one of the four sites and showing an allyl–ene distortion. The V—N—C angle is 169.1 (4) $^\circ$ . The crystal packing involves C—H $\cdots$ Cl interactions, with H $\cdots$ Cl distances in the range 2.87 (5)–2.89 (4)  $\text{\AA}$ .

**Comment**

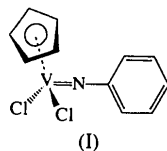
The chemistry of the half-sandwich vanadium imido system has recently been investigated due to the isolobal

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relationship between the [CpV(NR)] and [Cp<sub>2</sub>Ti] fragments (Buijink, Teuben, Kooijman & Spek, 1994; Chan, 1995). The title complex, (I), was prepared by the imido ligand exchange reaction between [CpV(N<sup>t</sup>Bu)Cl<sub>2</sub>] (Becker, Häusler & Preuss, 1987) and aniline.



The V—N1 distance of 1.653(4) Å and the small deviation from linearity of the V—N1—C1 angle [169.1(4)°] are typical for vanadium-terminal imido complexes (Mayer & Nugent, 1988) which exhibit multiple *pπ*–*dπ* interactions between the N and V atoms. The geometry around the metal centre is approximately tetrahedral due to the bulky nature of the Cp ring (Fig. 1). An allyl–ene distortion of this ring is evident (Table 1), with the metal displaced towards the C9 atom

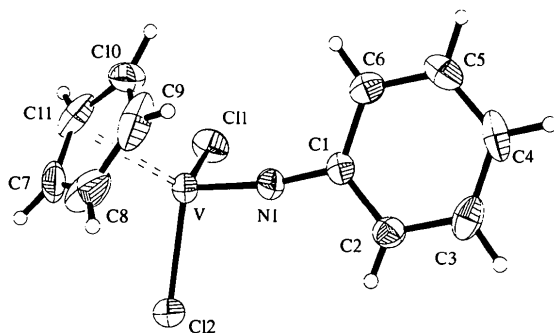


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids.

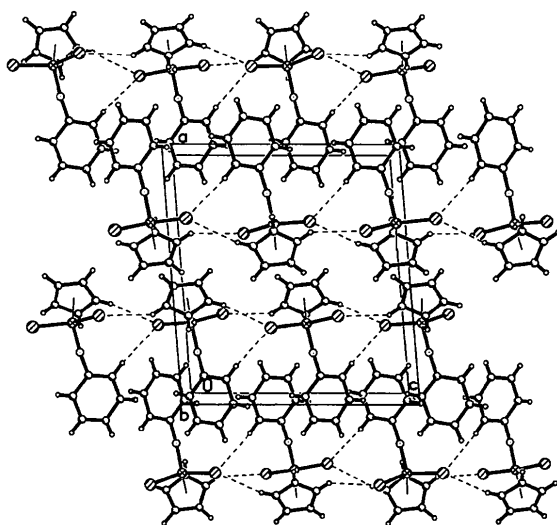


Fig. 2. The packing viewed along the *b* axis, showing H...Cl intermolecular interactions.

which eclipses the V—N bond. The distance from the centroid of the ring to the V atom is 1.968(6) Å.

The packing, with alternating layers of Cp rings and interleaved phenyl groups, is shown in Fig. 2. The C11...H8<sup>i</sup>, C12...H6<sup>ii</sup> and C12...H10<sup>ii</sup> intermolecular distances [2.88(6), 2.89(4) and 2.87(5) Å, respectively; symmetry codes: (i)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (ii)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ] are marginally less than the sum of the corresponding van der Waals radii (2.95 Å; Bondi, 1964); these secondary interactions presumably have a significant effect upon the observed packing arrangement.

## Experimental

Aniline (0.16 ml, 1.77 mmol) was added to a solution of [CpV(N<sup>t</sup>Bu)Cl<sub>2</sub>] (0.46 g, 1.77 mmol) in 1,2-dichloroethane (60 ml) at 243 K. After warming to room temperature, the mixture was heated to 333 K and stirred for two weeks. All volatile components were then removed from the dark red solution under reduced pressure to leave a red solid. Recrystallization of the solid with pentane and subsequent cooling at 268 K gave very dark purple crystals [yield: 0.23 g (47%)]. Elemental analysis for C<sub>11</sub>H<sub>10</sub>Cl<sub>2</sub>NV (278.05) found (required): C 47.46 (47.52), H 3.84 (3.63), N 4.69% (5.04%). IR data (Nujol, CsI, cm<sup>-1</sup>): 3070 (*w*), 2730 (*w*), 1600 (*m*, *br*), 1455 (*s*), 1415 (*m*), 1260 (*s*), 1095 (*s*), 1020 (*s*), 865 (*m*), 800 (*s*), 700 (*m*), 510 (*w*), 465 (*w*). <sup>1</sup>H NMR data (250 MHz, CDCl<sub>3</sub>, 298 K): 6.62 (*s*, 5H, C<sub>5</sub>H<sub>5</sub>), 6.7–7.2 (*m*, 5H, C<sub>6</sub>H<sub>5</sub>).

### Crystal data

[VCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>N)]

*M<sub>r</sub>* = 278.04

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 13.641(3) Å

*b* = 7.0340(10) Å

*c* = 12.403(2) Å

β = 94.66(3)°

*V* = 1186.1(4) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.557 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 24

reflections

θ = 10.10–13.77°

μ = 1.251 mm<sup>-1</sup>

*T* = 150(2) K

Block

0.30 × 0.25 × 0.08 mm

Very dark purple

### Data collection

Rigaku AFC-6S diffractometer

ω scans with profile analysis

(Lehmann & Larsen,

1974)

Absorption correction:

semi-empirical from ψ

scans (North, Phillips &

Mathews, 1968)

*T<sub>min</sub>* = 0.839, *T<sub>max</sub>* = 0.905

2821 measured reflections

2098 independent reflections

1244 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.0487

θ<sub>max</sub> = 25°

*h* = -16 → 16

*k* = -8 → 1

*l* = -1 → 14

3 standard reflections

every 150 reflections

intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>

*R*(*F*) = 0.0545

*wR*(*F*<sup>2</sup>) = 0.0905

$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 0.0179P]$

where  $P = (F_o^2 + 2F_c^2)/3$

S = 0.994

2098 reflections

166 parameters

H-atom coordinates refined;

U(H) = 1.2U<sub>eq</sub>(C) $(\Delta/\sigma)_{\max} = -0.067$  $\Delta\rho_{\max} = 0.405 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.351 \text{ e } \text{\AA}^{-3}$ 

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)*Acta Cryst.* (1997). **C53**, 204–206**Copper(II) and Nickel(II) Complexes of  
4-Methyl-4,7-diazadecane-1,10-diamine**TIAN-HUEY LU,<sup>a</sup> TAHIR H. TAHIROV,<sup>a</sup> KELUN SHU<sup>b</sup> AND  
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Table 1. Selected geometric parameters (Å, °)

V—N1	1.653 (4)	V—C9	2.236 (6)
V—Cl1	2.258 (2)	V—Cl10	2.246 (6)
V—Cl2	2.259 (2)	V—Cl11	2.354 (5)
V—C7	2.351 (5)	V—Cp†	1.968 (6)
V—C8	2.263 (6)		
N1—V—Cl1	99.72 (14)	Cl1—V—Cp	114.1 (8)
N1—V—Cl2	102.30 (14)	Cl2—V—Cp	113.5 (8)
Cl1—V—Cl2	103.65 (6)	N1—V—Cp	121.2 (7)
Cl1—N1—V	169.1 (4)		

† Cp is the centroid of the Cp ring.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: CF1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**References**

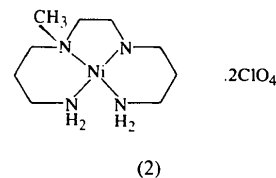
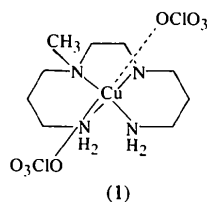
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**Abstract**

The X-ray crystal structures of (4-methyl-4,7-diazadecane-1,10-diamine-*N,N',N'',N'''*)(perchlorato-*O*)-copper(II) perchlorate, [Cu(C<sub>9</sub>H<sub>24</sub>N<sub>4</sub>)(ClO<sub>4</sub>)]ClO<sub>4</sub>, and (4-methyl-4,7-diazadecane-1,10-diamine-*N,N',N'',N'''*)-nickel(II) diperchlorate, [Ni(C<sub>9</sub>H<sub>24</sub>N<sub>4</sub>)](ClO<sub>4</sub>)<sub>2</sub>, are isomorphous with minor dissimilarities. The copper(II) complex is six-coordinate in a distorted octahedral geometry, with the four N atoms of the tetradentate ligand equatorial and the two O atoms of the perchlorate groups axial. The nickel(II) complex is four-coordinate in a square-planar geometry. In both complexes, the conformations of the three consecutive six-, five- and six-membered rings are chair, *gauche* and chair, respectively. In both crystals, hydrogen bonds involving the amino groups and perchlorate O atoms help stabilize the crystal structure.

**Comment**

The crystal structures of the copper(II) complex of *N,N'*-bis(3-aminopropyl)-1,2-ethanediamine and its associates have been reported previously (Lee *et al.*, 1986; Tahirov, Lu, Shu & Chung, 1994*a,b*, 1995). In order to investigate the steric effects of *N*-alkyl groups on the structures of the copper(II) and nickel(II) complexes, we have studied the crystal structures of the title complexes (4-methyl-4,7-diazadecane-1,10-diamine)(perchlorato-*O*)copper(II) perchlorate, (1), and (4-methyl-4,7-diazadecane-1,10-diamine)nickel(II) diperchlorate, (2).



The structure of the Ni<sup>II</sup> complex is isomorphous with that of the Cu<sup>II</sup> complex with minor dissimilarities. Appreciable electron-density residues were observed in the penultimate difference Fourier map. The occupan-