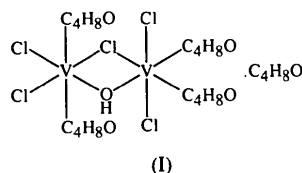


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Ziegler–Natta-type catalysts (Kahn, 1993; Poli & Torralba, 1993; Shaik, Hoffmann, Fisel & Summerville, 1980; Sobota *et al.*, 1995). Only a few examples of low-valent divanadium complexes are known, however, because of the lack of a useful synthetic method. Recently, Sobota and co-workers reported the synthesis, molecular structures and polymerization reactivity of two divanadium(III) complexes having two Cl bridges (Sobota, Ejfler, Szafert, Szczegot & Sawka-Dobrowolska, 1993; Sobota *et al.*, 1995). We obtained the asymmetric divanadium(III) complex having Cl and OH bridges from the reaction of  $[VCl_3(thf)_3]$  with  $NaCPh_3$  under an argon atmosphere. The structure of this complex, (I), was determined.



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## A Divanadium(III) Complex Bridged by $Cl^-$ and $OH^-$ Anions

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### Abstract

The crystal structure of the complex  $\mu$ -chloro- $\mu$ -hydroxo-bis[dichlorobis(tetrahydrofuran-*O*)vanadium(III)] tetrahydrofuran solvate,  $[V_2(\mu-Cl)(\mu-OH)Cl_4(thf)_4] \cdot thf$  (where thf is tetrahydrofuran,  $C_4H_8O$ ), was determined. It was obtained from a tetrahydrofuran solution containing  $[VCl_3(thf)_3]$  and  $NaCPh_3$ . The two octahedral vanadium(III) centers are bridged by a  $Cl^-$  and an  $OH^-$  anion, with a  $V \cdots V$  separation of 3.281 (1) Å. One vanadium(III) center has two axial Cl and two equatorial tetrahydrofuran ligands, while the other vanadium(III) center has two axial tetrahydrofuran and two equatorial Cl ligands. A tetrahydrofuran molecule which is contained as crystalline solvent is involved in hydrogen bonding with the bridging  $OH^-$  anion.

### Comment

Dinuclear metal complexes bridged by halogen atoms or hydroxy groups have been extensively studied with regard to metal–metal magnetic interactions, stereoisomerism and stereoselective reactivity, and their use as

An *ORTEP*II (Johnson, 1976) drawing of (I) is shown in Fig. 1. Two vanadium(III) centers based on the octahedron are linked by Cl and OH bridges. The V(1) atom has two axial Cl atoms and two equatorial tetrahydrofuran molecules, while V(2) has two axial tetrahydrofuran molecules and two equatorial Cl atoms. Thus, the configurations of both vanadium(III) centers are different. The V(1)—O(2) and V(1)—O(3) bond distances [2.024 (4) and 2.030 (4) Å, respectively] are shorter than the V(2)—O(4) and V(2)—O(5) bond distances [2.088 (4) and 2.100 (4) Å, respectively], indicating that axial tetrahydrofuran ligation results in a stronger V—O bond compared with equatorial ligation.

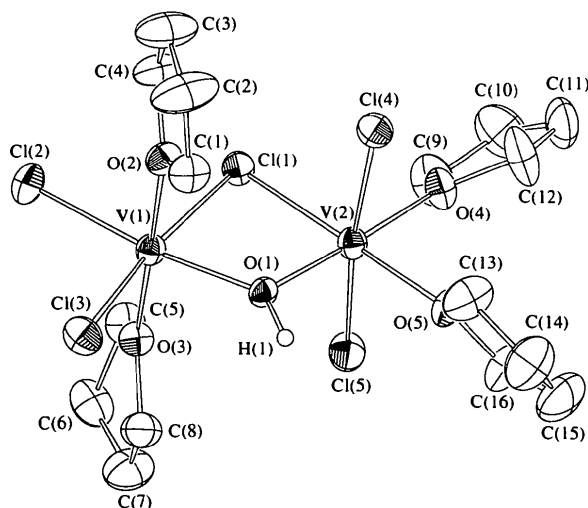


Fig. 1. An *ORTEP*II view of (I) with the atom-numbering scheme and ellipsoids plotted at the 30% probability level. H atoms of the tetrahydrofuran ligands have been omitted for clarity and the tetrahydrofuran solvate molecule is not shown.

Since all axial ligations of tetrahydrofuran molecules are sterically undesirable, the present configuration, *i.e.* two axial and two equatorial, was formed.

The V(1)—Cl(1) [2.466 (2) Å] and V(1)—O(1) [1.974 (4) Å] bond distances are longer than the respective V(2)—Cl(1) [2.411 (2) Å] and V(2)—O(1) [1.923 (4) Å] distances. This is due to the stronger *trans* influence of the Cl ligands compared with the coordinating tetrahydrofuran molecules. These bond lengths afford a smaller Cl(1)—V(1)—O(1) bond angle of 79.2 (1)° compared with the Cl(1)—V(2)—O(1) angle of 81.6 (1)°. The V(1)—Cl(1)—V(2) bond angle [84.56 (6)°] is much smaller than V(1)—O(1)—V(2) [114.7 (2)°] and as a result the V(1)—Cl(1)—V(2)—O(1) square deviates greatly from  $D_{4h}$  symmetry. The V...V separation of 3.281 (1) Å indicates no direct vanadium–vanadium interaction. The complex has a tetrahydrofuran molecule as a crystalline solvent, which forms a hydrogen bond to the bridging hydroxy group [O(1)...O(6) 2.669 (5) Å]. The source of the hydroxy group is likely to be contaminated air or moisture.

Sobota and co-workers have shown that divanadium(III) complexes bridged by two Cl ligands [Cl<sub>2</sub>(L)<sub>2</sub>V(μ-Cl)<sub>2</sub>V(L)<sub>2</sub>Cl<sub>2</sub>] (L = tetrahydrofuran, ethyl acetate) have axial–equatorial tetrahydrofuran (or ethyl acetate) ligations on both vanadium(III) centers. These complexes have crystallographic  $C_i$  symmetry (Sobota *et al.*, 1993, 1995). The difference in configuration between the complexes of Sobota and co-workers and that of complex (I) is probably due to the effect of the OH bridge of (I).

## Experimental

A tetrahydrofuran solution of [VCl<sub>3</sub>(thf)<sub>3</sub>] (Manzer, 1982) was added to a diethyl ether solution containing NaCPh<sub>3</sub> at 183 K and stirred for 4 h. After the reaction temperature was raised to room temperature, the solution was stirred overnight. The brownish solution obtained was filtered and allowed to stand for 2 d at 263 K, whereupon air-sensitive brownish single crystals of (I) were obtained. The crystal used for analysis was mounted on the end of a 0.30 mm glass capillary tube with mother liquor.

### Crystal data

[V<sub>2</sub>Cl<sub>5</sub>(OH)(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub>].-  
C<sub>4</sub>H<sub>8</sub>O

$M_r = 656.69$

Monoclinic

$P2_1/n$

$a = 9.324 (3) \text{ \AA}$

$b = 16.590 (5) \text{ \AA}$

$c = 18.978 (2) \text{ \AA}$

$\beta = 90.39 (2)^\circ$

$V = 2935 (1) \text{ \AA}^3$

$Z = 4$

$D_x = 1.486 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25  
reflections

$\theta = 20.53\text{--}27.91^\circ$

$\mu = 1.122 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plate

$0.30 \times 0.20 \times 0.10 \text{ mm}$

Brown

### Data collection

Rigaku AFC-7R diffractometer

$\omega/2\theta$  scans

Absorption correction:

empirical *via*  $\psi$  scan

(North, Phillips &

Mathews, 1968)

$T_{\min} = 0.843$ ,  $T_{\max} =$

0.996

7515 measured reflections

7033 independent reflections

### Refinement

Refinement on  $F$

$R = 0.047$

$wR = 0.032$

$S = 1.80$

2753 reflections

302 parameters

$w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{\max} < 0.001$

2753 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 27.56^\circ$

$h = 0 \rightarrow 12$

$k = 0 \rightarrow 19$

$l = -23 \rightarrow 23$

3 standard reflections

monitored every 150

reflections

intensity decay: 17.15%

$\Delta\rho_{\max} = 0.377 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.356 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
V(1)	0.7854 (1)	0.24306 (6)	0.82994 (5)	0.0423 (3)
V(2)	0.6287 (1)	0.22320 (6)	0.67559 (5)	0.0440 (3)
Cl(1)	0.6069 (2)	0.14700 (9)	0.78315 (8)	0.0503 (5)
Cl(2)	0.7809 (2)	0.17968 (10)	0.93964 (8)	0.0644 (6)
Cl(3)	0.9574 (2)	0.33978 (9)	0.85943 (9)	0.0627 (6)
Cl(4)	0.4282 (2)	0.29865 (9)	0.70743 (8)	0.0601 (6)
Cl(5)	0.8105 (2)	0.13984 (10)	0.63103 (9)	0.0630 (6)
O(1)	0.7636 (4)	0.2827 (2)	0.7324 (2)	0.039 (1)
O(2)	0.6274 (4)	0.3183 (2)	0.8615 (2)	0.050 (1)
O(3)	0.9435 (4)	0.1664 (2)	0.8002 (2)	0.049 (1)
O(4)	0.4880 (4)	0.1482 (2)	0.6201 (2)	0.058 (2)
O(5)	0.6491 (4)	0.2977 (2)	0.5867 (2)	0.055 (1)
O(6)	0.4533 (5)	0.1305 (3)	0.1599 (3)	0.087 (2)
C(1)	0.6206 (7)	0.4037 (4)	0.8458 (3)	0.062 (2)
C(2)	0.4952 (9)	0.4344 (5)	0.8819 (5)	0.118 (4)
C(3)	0.4201 (8)	0.3694 (5)	0.9112 (5)	0.105 (4)
C(4)	0.4977 (7)	0.2951 (4)	0.8967 (4)	0.070 (3)
C(5)	0.9384 (7)	0.0793 (3)	0.8052 (3)	0.062 (2)
C(6)	1.0871 (8)	0.0519 (4)	0.7985 (4)	0.076 (3)
C(7)	1.1553 (7)	0.1139 (5)	0.7538 (4)	0.091 (3)
C(8)	1.0764 (7)	0.1884 (4)	0.7659 (3)	0.065 (2)
C(9)	0.4920 (8)	0.0619 (4)	0.6208 (4)	0.083 (3)
C(10)	0.3686 (9)	0.0345 (5)	0.5830 (5)	0.115 (4)
C(11)	0.2999 (9)	0.1032 (6)	0.5475 (4)	0.101 (4)
C(12)	0.3749 (9)	0.1728 (4)	0.5738 (4)	0.102 (3)
C(13)	0.6098 (8)	0.3814 (4)	0.5837 (4)	0.091 (3)
C(14)	0.6602 (10)	0.4126 (5)	0.5169 (5)	0.106 (4)
C(15)	0.7004 (9)	0.3446 (6)	0.4734 (4)	0.115 (4)
C(16)	0.7031 (8)	0.2745 (4)	0.5191 (4)	0.084 (3)
C(17)	0.478 (1)	0.0513 (5)	0.1813 (5)	0.138 (4)
C(18)	0.5543 (10)	0.0129 (5)	0.1271 (5)	0.122 (4)
C(19)	0.6218 (9)	0.0772 (5)	0.0875 (5)	0.117 (4)
C(20)	0.5622 (8)	0.1516 (4)	0.1152 (4)	0.078 (3)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

V(1)—Cl(1)	2.466 (2)	V(2)—Cl(4)	2.333 (2)
V(1)—Cl(2)	2.333 (2)	V(2)—Cl(5)	2.349 (2)
V(1)—Cl(3)	2.334 (2)	V(2)—O(1)	1.923 (4)
V(1)—O(1)	1.974 (4)	V(2)—O(4)	2.088 (4)
V(1)—O(2)	2.024 (4)	V(2)—O(5)	2.100 (4)
V(1)—O(3)	2.030 (4)	O(1)—O(6')	2.669 (5)
V(2)—Cl(1)	2.411 (2)		

Cl(1)—V(1)—Cl(2)	90.80 (6)	Cl(1)—V(2)—Cl(5)	93.52 (6)
Cl(1)—V(1)—Cl(3)	172.68 (7)	Cl(1)—V(2)—O(1)	81.6 (1)
Cl(1)—V(1)—O(1)	79.2 (1)	Cl(1)—V(2)—O(4)	93.3 (1)
Cl(1)—V(1)—O(2)	90.8 (1)	Cl(1)—V(2)—O(5)	175.5 (1)
Cl(1)—V(1)—O(3)	89.1 (1)	Cl(4)—V(2)—Cl(5)	172.05 (7)
Cl(2)—V(1)—Cl(3)	96.44 (7)	Cl(4)—V(2)—O(1)	95.8 (1)
Cl(2)—V(1)—O(1)	170.0 (1)	Cl(4)—V(2)—O(4)	87.1 (1)
Cl(2)—V(1)—O(2)	89.8 (1)	Cl(4)—V(2)—O(5)	88.2 (1)
Cl(2)—V(1)—O(3)	89.0 (1)	Cl(5)—V(2)—O(1)	91.9 (1)
Cl(3)—V(1)—O(1)	93.6 (1)	Cl(5)—V(2)—O(4)	85.4 (1)
Cl(3)—V(1)—O(2)	90.3 (1)	Cl(5)—V(2)—O(5)	89.3 (1)
Cl(3)—V(1)—O(3)	89.9 (1)	O(1)—V(2)—O(4)	174.1 (2)
O(1)—V(1)—O(2)	90.1 (1)	O(1)—V(2)—O(5)	94.9 (2)
O(1)—V(1)—O(3)	91.0 (2)	O(4)—V(2)—O(5)	90.3 (2)
O(2)—V(1)—O(3)	178.8 (2)	V(1)—Cl(1)—V(2)	84.56 (6)
Cl(1)—V(2)—Cl(4)	89.40 (6)	V(1)—O(1)—V(2)	114.7 (2)

Symmetry code: (i)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .

The weak reflections [ $I < 10\sigma(I)$ ] were rescanned (maximum of two rescans) and the counts accumulated to insure good counting statistics. The structure was solved by direct methods using the *SIR88* program (Burla *et al.*, 1989) and expanded using Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992). The position of the H(1) atom was determined from the difference Fourier synthesis map and refined isotropically. Other H atoms were placed in calculated positions (C—H = 1.08 Å). The non-H atoms were refined anisotropically. All H atoms, except for H(1), were included but not refined. All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985, 1992). *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) was used for data collection and cell refinement.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## A New Allotropic Form of *trans*-Dichlorobis(creatinine)platinum(II) Dihydrate

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### Abstract

The synthesis and crystal structure of a new allotropic form (violet crystals) of *trans*-bis(2-amino-1-methyl-1,5-dihydro-4*H*-imidazol-4-one-*N*<sup>1</sup>)dichloroplatinum(II), [PtCl<sub>2</sub>(C<sub>4</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>2</sub>].2H<sub>2</sub>O, are reported. This form differs from the two crystal forms (yellow and green crystals) studied previously in its intermolecular hydrogen-bonding scheme. The crystal structure of the new form is isomorphous with that reported for the corresponding palladium complex, *trans*-[PdCl<sub>2</sub>(C<sub>4</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>2</sub>].2H<sub>2</sub>O.

### Comment

The anticancer properties of the drug cisplatin, *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>], have motivated us to investigate the coordination chemistry of platinum–creatinine complexes. These compounds have potential antitumour activity and low nephrotoxicity compared with the anticancer drug cisplatin. Creatinine (2-amino-1-methyl-1,5-dihydro-4*H*-imidazol-4-one) plays an important role in protein metabolism and is of considerable biological interest. It has more than one site capable of coordinating to metal ions and, similar to adenine (Hodgson, 1977), can form cationic, neutral and anionic metal complexes. The syntheses of platinum–creatinine complexes and their properties have been described by Martín-Gil & Martín-Gil (1987). We have reported previously (Matos Beja, Paixão, Martín-Gil & Salgado, 1991) the crystal structures of two allotropic forms of PtCl<sub>2</sub>(creatinine)<sub>2</sub>, (I), corresponding to yellow and green crystals, formed by the reaction of K<sub>2</sub>PtCl<sub>4</sub> and creatinine in aqueous solution at room temperature. The X-ray analyses have

