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Chlorobis{2-[(dimethylamino)methyl]-phenyl-C^1,N}(pyridine)vanadium(III)

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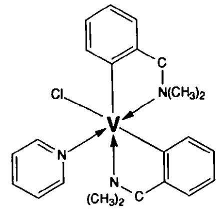
Abstract

The octahedral coordination of the tervalent bis-aryl vanadium complex [$VCl(C_5H_5N)(C_9H_{12}N)_2$] is completed by one pyridine and one Cl ligand with a V—Cl distance of 2.395 (2) Å.

Comment

Divalent and tervalent vanadium ions play a significant role in biological systems (Robson *et al.*, 1986). Nitrogen fixation and reduction (Denisov, Efimov, Shuvalova, Shilova & Shilov, 1970; Shilov *et al.*, 1971) is an important phenomenon with regard to the activity of V^{II} and V^{III} and has been studied by a number of research groups.

The presence of either alkoxo or alkyl groups in the coordination sphere of the V atom may account for this particular type of activity of the transition metal. In a previous report, we described the formation of a V^{II} dinitrogen complex (Edema, Gambarotta & Meetsma, 1989) bearing *ortho*-dimethylaminomethylphenyl ligands (o-$Me_2NCH_2C_6H_4$). The highly reductive power of this complex was investigated by oxidation chemistry. We found that the dinitrogen species [{$V(o\text{-}Me_2CH_2C_6H_4)_2(py)$}$_2(\mu\text{-}N_2)$] reacted smoothly with one equivalent of CuCl to release dinitrogen and concomittantly form the tervalent title compound (I), [$VCl(o\text{-}Me_2CH_2C_6H_4)_2(py)$], as a deep-red crystalline solid.



(I)

The geometry of the present V^{III} chlorine complex (Fig. 1) resembles closely that of its V^{II} dinitrogen precursor. However, comparable V—C bonds are now significantly shorter, *e.g.* the bond *trans* to Cl is 2.125 (5) Å compared to 2.204 (4) Å for the bond *trans* to dinitrogen.

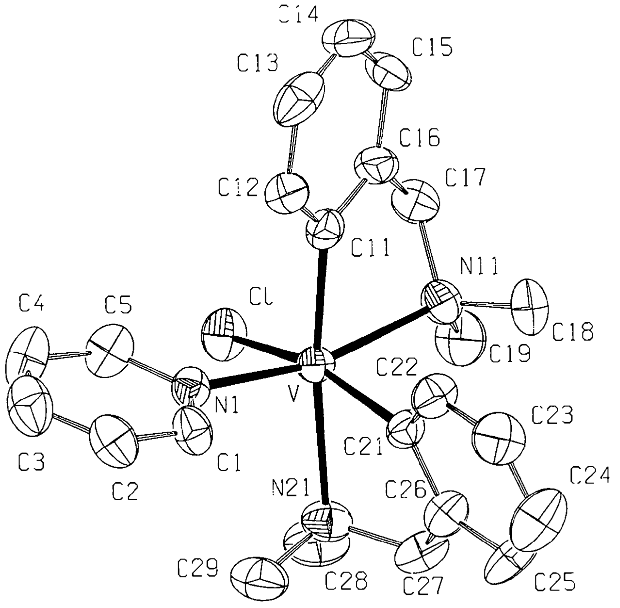


Fig. 1. View of the title complex with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted.

Experimental

Crystals of a quality suitable for X-ray analysis were obtained directly from the reaction mixture.

Crystal data

[$VCl(C_5H_5N)(C_9H_{12}N)_2$]
$M_r = 433.90$
Orthorhombic
$P2_12_12_1$
$a = 8.283$ (3) Å
$b = 15.706$ (3) Å
$c = 16.990$ (3) Å
$V = 2210.3$ (10) Å^3
$Z = 4$
$D_x = 1.304$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 17 reflections
$\theta = 7$–$11°$
$\mu = 0.57$ mm^{-1}
$T = 295$ K
Needle
0.40 × 0.15 × 0.12 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans [$\Delta\omega = (0.80 + 0.35\tan\theta)°$]
Absorption correction: none
4349 measured reflections
3885 independent reflections
2454 observed reflections [$I > 2.5\sigma(I)$]

$R_{\rm int} = 0.055$
$\theta_{\rm max} = 25.0°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 18$
$l = -20 \rightarrow 20$
2 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
$R = 0.046$
$wR = 0.034$
$S = 1.19$
2454 reflections
267 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.000102F^2]$
$(\Delta/\sigma)_{\rm max} = 0.08$
$\Delta\rho_{\rm max} = 0.43$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.42$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
V	0.38722 (10)	0.48582 (5)	0.19018 (4)	0.0305 (3)
Cl	0.55227 (16)	0.54551 (8)	0.29188 (7)	0.0468 (5)
N1	0.5792 (5)	0.5041 (3)	0.10322 (19)	0.0340 (16)
N11	0.1707 (5)	0.5001 (3)	0.2736 (2)	0.0407 (16)
N21	0.4819 (6)	0.3498 (3)	0.2310 (2)	0.0430 (17)
C1	0.5807 (6)	0.4647 (3)	0.0336 (3)	0.041 (2)
C2	0.6966 (6)	0.4794 (4)	−0.0234 (3)	0.050 (2)
C3	0.8157 (7)	0.5382 (4)	−0.0094 (3)	0.060 (3)
C4	0.8134 (8)	0.5814 (4)	0.0604 (3)	0.062 (3)
C5	0.6924 (7)	0.5632 (3)	0.1150 (3)	0.049 (2)
C11	0.2724 (7)	0.5955 (3)	0.1459 (3)	0.0350 (19)
C12	0.2887 (7)	0.6359 (3)	0.0730 (3)	0.046 (2)
C13	0.2040 (8)	0.7102 (4)	0.0548 (3)	0.057 (3)
C14	0.1029 (8)	0.7468 (3)	0.1104 (4)	0.060 (3)
C15	0.0839 (6)	0.7086 (3)	0.1823 (3)	0.049 (2)
C16	0.1669 (6)	0.6348 (3)	0.2001 (3)	0.0413 (17)
C17	0.1523 (7)	0.5939 (3)	0.2794 (3)	0.050 (2)
C18	0.0188 (6)	0.4650 (3)	0.2405 (3)	0.054 (3)
C19	0.1886 (7)	0.4661 (4)	0.3543 (3)	0.060 (2)
C21	0.2601 (7)	0.3981 (3)	0.1179 (3)	0.0340 (19)
C22	0.1698 (7)	0.4142 (3)	0.0493 (3)	0.0433 (19)
C23	0.0781 (7)	0.3545 (4)	0.0110 (3)	0.057 (3)
C24	0.0740 (9)	0.2728 (4)	0.0389 (3)	0.071 (3)
C25	0.1621 (8)	0.2522 (3)	0.1048 (3)	0.061 (3)
C26	0.2548 (7)	0.3131 (3)	0.1433 (3)	0.0447 (19)
C27	0.3436 (7)	0.2921 (3)	0.2188 (3)	0.052 (2)
C28	0.5387 (8)	0.3382 (3)	0.3121 (3)	0.063 (2)
C29	0.6107 (8)	0.3216 (3)	0.1775 (3)	0.059 (2)

Table 2. *Selected geometric parameters* (Å, °)

V—Cl	2.3945 (17)	N1—C5	1.334 (7)
V—N1	2.190 (4)	N11—C17	1.484 (7)
V—N11	2.297 (4)	N11—C18	1.485 (6)
V—N21	2.379 (5)	N11—C19	1.479 (6)
V—C11	2.107 (5)	N21—C27	1.475 (7)
V—C21	2.125 (5)	N21—C28	1.467 (6)
N1—C1	1.335 (6)	N21—C29	1.470 (7)
Cl—V—N1	91.20 (11)	N1—V—C21	93.15 (18)
Cl—V—N11	87.84 (10)	N11—V—N21	99.51 (16)
Cl—V—N21	87.31 (11)	N11—V—C11	77.76 (19)
Cl—V—C11	101.26 (15)	N11—V—C21	91.89 (19)
Cl—V—C21	162.52 (14)	N21—V—C11	170.83 (19)
N1—V—N11	166.09 (17)	N21—V—C21	75.50 (17)
N1—V—N21	94.30 (16)	C11—V—C21	95.7 (2)
N1—V—C11	88.84 (19)		

X-ray data were collected for a crystal mounted inside a Lindemann glass capillary using locally modified CAD-4 software. Cell refinement was performed with *SET*4 (de Boer & Duisenberg, 1984); data reduction with *HELENA* (Spek, 1993). The structure was solved by Patterson techniques and subsequent difference Fourier analysis (*SHELXS*86; Sheldrick, 1985). H atoms were included riding on their carrier atoms with two common isotropic displacement parameters. *SHELX*76 (Sheldrick, 1976) was used for refinement. The absolute structure with the lower R value was adopted ($R = 0.046$ *cf.* 0.049; $wR = 0.035$ *cf.* 0.039). Molecular graphics were produced using *PLATON* (Spek, 1990).

We thank Dr J. L. de Boer for making his CAD-4 available across the National network for remotely controlled data collection. This work was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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{1,3,5,7-Tetraazabicyclo[3.3.1]nonane-3,7-bis(acetato)-N^3,N^7,*O*,*O''*}nickel(II)

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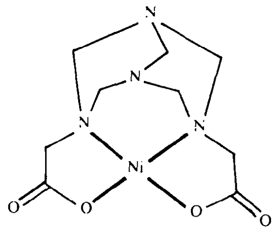
Abstract

The structure of the title compound, $[Ni(C_9H_{14}N_4O_4)]$ has been redetermined in the centrosymmetric space group *Pnma*. The Ni^{II} atom is coordinated by two N and two O atoms of the ligand in an approximately square-planar arrangement.

Comment

The structure has been solved by Teo, Teoh & Snow (1984) in the non-centrosymmetric space group $Pna2_1$; the ligating atoms and Ni were found to lie in a pseudo-mirror plane of this space group. We performed the usual statistical test based on normalized structure factors, *E* (Stout & Jensen, 1989), on our data and found that the title compound is centrosymmetric ($|E^2 - 1| = 0.917$). Therefore, it was possible to solve the structure of this compound in the space group *Pnma*.



$Ni^{II}L$

The structure is composed of isolated molecules of the $Ni^{II}L$ complex; no evidence of hydrogen bonding was found. A perspective view of the molecule is given in Fig. 1. The Ni^{II} atom is coordinated by two N atoms and two O atoms of the ligand molecule in a slightly deformed square-planar arrangement, in a mirror plane of the space group *Pnma*.

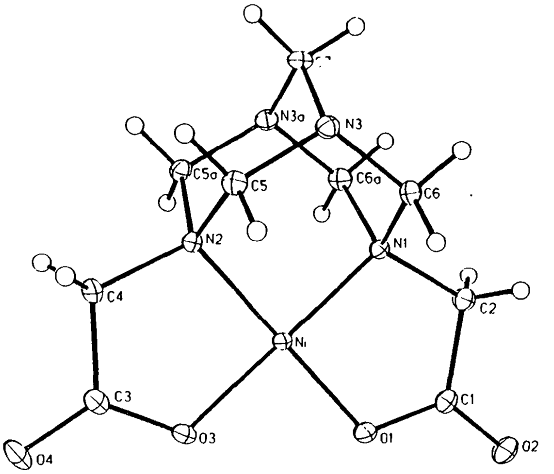


Fig. 1. View of a molecule of the $Ni^{II}L$ complex. The non-H atoms are represented by displacement ellipsoids at the 50% probability level. The H atoms have been assigned arbitrary displacement parameters.

Experimental

The new complex of general formula $Ni^{II}L$ (where L^{2-} is the macrocyclic ligand $C_9H_{14}N_4O_4$) was prepared by template condensation of $[Ni(H_2O)_2(gly)_2]$ (where gly is glycine) with formaldehyde and ammonia. The preparation and physicochemical study of the compound $Ni^{II}L$ have been described previously (Trávníček, Březina, Krausová & Šindelář, 1993). The compound was recrystallized from water.

Crystal data

$[Ni(C_9H_{14}N_4O_4)]$
$M_r = 300.9$
Orthorhombic
Pnma
$a = 10.618$ (2) Å
$b = 6.735$ (1) Å
$c = 14.683$ (3) Å
$V = 1050.0$ (3) Å^3
$Z = 4$
$D_x = 1.904$ Mg m^{-3}
$D_m = 1.87$ Mg m^{-3}
D_m measured by flotation in $CHCl_3/CH_3I$ at 293 K

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 27.5–43.5°$
$\mu = 2.804$ mm^{-1}
$T = 293$ K
Needle
0.65 × 0.1 × 0.1 mm
Orange

Data collection

Kuma KM-4 diffractometer
ω–2θ scans
Absorption correction: none
1571 measured reflections
1199 independent reflections
1029 observed reflections [$I > 5\sigma(I)$]
$R_{int} = 0.0171$

$\theta_{max} = 83°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 18$
2 standard reflections monitored every 50 reflections
intensity variation: 10%