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# Niobium 1,4-Diazabutadiene Derivatives. Structure of ($\eta^5$-Cp)NbCl$_2$($^t$BuNCH-CHN$^t$Bu)

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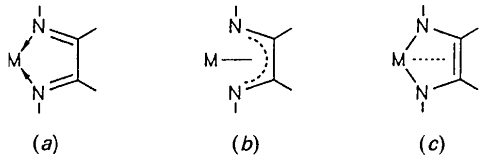
## Abstract

Crystals of dichloro($\eta^5$-cyclopentadienyl)(*N*,*N*′-di-*tert*-butyl-1,2-ethanediimine-*N*,*N*′)niobium were obtained by ligand exchange reaction between CpNbCl$_2$(PMe$_3$)$_3$ and $^t$BuN=CH—CH=N$^t$Bu. The structure shows pseudo-octahedral coordination around the metal, with the chlorine ligands in *cis* positions relative to each other. The diimine ligand has an $\eta^2$-coordination mode with the five-membered metallacyclic ring adopting an envelope conformation. The long C—N distance together with the short C—C one imply electronic delocalization over the chelate. The conformation of the chelate leads to short Nb—C bonds and the $\sigma^2,\pi$-metallacyclopentene character of the diimine ligand reduces the electron deficiency of the metal.

## Comment

1,4-Diazabutadiene ligands, *R*N=CH—CH=N*R* (*R*-dab), have been shown to exhibit a diverse coordination chemistry as a result of their steric and electronic flexibility (Vrieze & Van Koten, 1985; Van Koten & Vrieze, 1982). However, studies have mostly involved later transition metals and few reports concern early transition metals (Scholz, Dietrich, Schuman & Thiele, 1991; Scholz, Dlikan, Stöhl, Dietrich, Schuman & Thiele, 1990; Woitha, Behrens, Vergopoulos & Rehder, 1990). No reaction between a niobium or tantalum derivative and 1,4-diazabutadiene ligands has been reported to our knowledge. Since these ligands have been shown to be able to stabilize low formal oxidation states, we have investigated their behaviour towards niobium and tantalum species in various oxidation states. The reaction between ($\eta^5$-Cp)NbCl$_2$(PMe$_3$)$_3$ and di-*tert*-butylethanediimine offered ($\eta^5$-Cp)NbCl$_2$-($^t$BuNC$_2$H$_2$N$^t$Bu). Its structure was investigated by X-ray diffraction in order to determine precisely the coordination mode of the versatile nitrogen ligand, which may adopt a large variety of forms, although types (*a*) to (*c*) are the most likely for the compound under study.



(*a*) (*b*) (*c*)

($\eta^5$-Cp)NbCl$_2$($^t$BuNCHCHN$^t$Bu) has been obtained by the ligand-exchange reaction (photochemically activated) between CpNbCl$_2$(PMe$_3$)$_3$ (Zaki, Hubert-Pfalzgraf & Toupet, 1991) and di-*tert*-butylethanediimine. Crystals suitable for X-ray analysis were obtained from the reaction medium. The compound crystallizes as discrete molecules. The overall structure corresponds to a piano-stool geometry with the chlorine ligands in *cis* positions, as found, for example, for CpNbCl$_2$(dmpe) (dmpe = dimethylphosphinoethane) (Holloway & Melnik, 1986). The Nb—Cl bond lengths (2.516 Å av.) are in agreement with the data reported for other Nb$^{\rm III}$

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adducts (Hubert-Pfalzgraf, Postel & Riess, 1987). The diazabutadiene ligands display a $\sigma,\sigma$-*N*,*N'* chelating behaviour with a bite angle of 84.7 (2)°; it is thus a 4 e donor and the resulting niobium derivative is a 16 e species.

Monocyclopentadienyl derivatives of niobium or tantalum with nitrogen donors are limited to $[(R\mathrm{Cp})\mathrm{NbCl_2}(LL)]_2(\mu\text{-O})$ ($R$ = H, Me, SiMe$_3$; $LL$ = 2,2′-bipyridine, *o*-phenanthroline) derivatives, but no structural data are available (Reu, Jalon & Otero, 1988). Diazadiene ligands have been formed by the dimerization of isocyanides in the coordination sphere of Nb$^{\mathrm{III}}$ or Ta$^{\mathrm{III}}$ complexes. The Nb—N(1)—C(6)—C(7)—N(2) unit of $(\eta^5\text{-Cp})\mathrm{NbCl_2}(^t\mathrm{Nu}\text{-dab})$ is related to that of $\mathrm{Nb_2Cl_6}(^t\mathrm{BuNC})_6$ (Cotton, Duraj & Roth, 1984) although the diazabutadiene is a tetradentate ligand in the latter. The average Nb—N bond length of 2.017 Å is close to that observed for $\sigma$ bonds, such as for [Nb(NMe$_2$)$_5$], and thus are much shorter than the values usually found for Nb$^{\mathrm{III}}$ adducts such as $[\mathrm{Nb_2}(\mu\text{-Cl})_2\mathrm{Cl_4}(\eta^2\text{-Et_2NC_2H_4NEt_2})]$ [2.44 Å av. (Canich & Cotton, 1987)]. The C—N (1.358 Å av.) and C—C distances [1.403 (7) Å av.] imply partial electronic delocalization over the chelate. Indeed, in a true 1,4-diazabutadiene complex such as $[\mathrm{PtCl_2}(\mu\text{-styrene})(^t\mathrm{BuN{=}CHCH{=}N}^t\mathrm{Bu})]$ (Vrieze & Van Koten, 1985), the C—N distances are short [1.28 (3) Å], indicative of double-bond character, while the C—C distances are long [1.51 (5) Å], consistent with essentially single-bond character. This $\pi$ delocalization seems to be a general feature, although its intensity is variable, of low-valent early transition-metal derivatives (Hessen, Bol, de Boer, Meetsma & Teuben, 1989; Chisholm, Folting, Huffman & Koh, 1989) as a way of reducing their electron-deficient character. The five-membered metallacyclic ring Nb—N(1)—C(6)—C(7)—N(2) unit is essentially folded with a dihedral angle between Nb—N(1)—N(2) and N(1)—N(2)—C(6)—C(7) of 66.2°, which also leads to short Nb—C(6) and Nb—C(7) distances (≃2.40 Å). These data support a coordination mode of type (*c*) and thus a $\sigma^2,\pi$-azametallacyclopentene character as observed, for instance, for $(\eta^5\text{-Cp})\mathrm{TiCl}(R\text{-dab})$ ($R$ = CH$_2$Ph) (Scholz, Dietrich, Schuman & Thiele, 1991). The mean Nb—C(Cp) bond distance (2.41 Å) is in agreement with the data reported in the literature for either mono- or biscyclopentadienyl niobium derivatives (Holloway & Melnik, 1986).

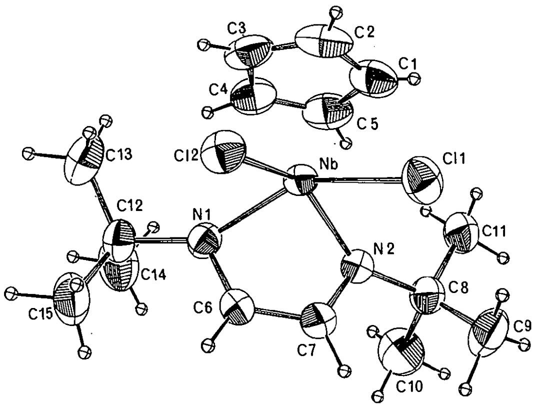

Fig. 1. View of the title molecule with the atom-labelling scheme.

## Experimental

*Crystal data*

$[\mathrm{NbCl_2(C_5H_5)(C_{10}H_{20}N_2)}]$
$M_r$ = 379.2
Monoclinic
$P2_1/n$
$a$ = 9.888 (4) Å
$b$ = 13.827 (3) Å
$c$ = 13.307 (6) Å
$\beta$ = 107.31 (4)°
$V$ = 1737 (1) Å$^3$
$Z$ = 4
$D_x$ = 1.52 Mg m$^{-3}$

Mo *K*$\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 9–12°
$\mu$ = 0.967 mm$^{-1}$
$T$ = 294 K
Prism
0.24 × 0.14 × 0.12 mm
Red-brown

*Data collection*

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\mathrm{min}}$ = 0.723, $T_{\mathrm{max}}$ = 1.353
4175 measured reflections
1653 independent reflections

1653 observed reflections [$I > 5\sigma(I)$]
$R_{\mathrm{int}}$ = 0.020
$\theta_{\mathrm{max}}$ = 25°
$h$ = 0 → 12
$k$ = 0 → 17
$l$ = −17 → 17
3 standard reflections
frequency: 60 min
intensity variation: 0.15%

*Refinement*

Refinement on $F^2$
Final $R$ = 0.030
$wR$ = 0.028
$S$ = 1.20
1653 reflections
257 parameters
Only coordinates of H atoms refined

$w = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$
$(\Delta/\sigma)_{\mathrm{max}}$ = 0.80
$\Delta\rho_{\mathrm{max}}$ = 0.45 e Å$^{-3}$
$\Delta\rho_{\mathrm{min}}$ = 0.05 e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Computations used the *Enraf–Nonius Structure Determination Package* (Frenz, 1985).

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

$$B_{\mathrm{eq}} = (4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)].$$

| | $x$ | $y$ | $z$ | $B_{\mathrm{eq}}$ |
|---|---|---|---|---|
| Nb | −0.03912 (4) | −0.20872 (3) | −0.10440 (3) | 2.660 (8) |
| Cl1 | −0.0156 (2) | −0.2113 (1) | 0.08829 (9) | 4.07 (3) |
| Cl2 | 0.2210 (1) | −0.17075 (9) | −0.0256 (1) | 3.63 (3) |
| N1 | −0.0242 (4) | −0.1165 (3) | −0.2178 (3) | 3.17 (8) |
| N2 | −0.2278 (3) | −0.1439 (3) | −0.1212 (3) | 3.13 (8) |

| | | | | |
|---|---|---|---|---|
| C1 | −0.1204 (6) | −0.3712 (4) | −0.0935 (4) | 4.8 (1) |
| C2 | 0.0270 (6) | −0.3746 (4) | −0.0760 (4) | 5.0 (1) |
| C3 | 0.0552 (5) | −0.3494 (4) | −0.1678 (4) | 4.8 (1) |
| C4 | −0.0714 (6) | −0.3284 (4) | −0.2434 (4) | 4.6 (1) |
| C5 | −0.1803 (5) | −0.3424 (4) | −0.1977 (4) | 4.8 (1) |
| C6 | −0.0556 (5) | −0.0427 (3) | −0.1617 (3) | 3.3 (1) |
| C7 | −0.1598 (4) | −0.0570 (3) | −0.1111 (3) | 3.3 (1) |
| C8 | −0.3705 (5) | −0.1437 (3) | −0.1017 (4) | 3.8 (1) |
| C9 | −0.3570 (5) | −0.1029 (4) | 0.0088 (4) | 5.3 (1) |
| C10 | −0.4675 (5) | −0.0813 (5) | −0.1856 (5) | 6.1 (2) |
| C11 | −0.4287 (5) | −0.2460 (4) | −0.1103 (4) | 4.8 (1) |
| C12 | 0.0401 (5) | −0.0928 (4) | −0.3034 (3) | 3.8 (1) |
| C13 | 0.1427 (6) | −0.1723 (5) | −0.3125 (4) | 5.8 (1) |
| C14 | −0.0846 (6) | −0.0866 (5) | −0.4034 (4) | 5.7 (1) |
| C15 | 0.1198 (6) | 0.0025 (4) | −0.2825 (5) | 5.4 (1) |

Table 2. *Selected bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Nb—Cl1 | 2.505 (1) | Nb—C2 | 2.385 (6) |
| Nb—Cl2 | 2.527 (1) | Nb—C3 | 2.416 (6) |
| Nb—N1 | 2.015 (4) | Nb—C4 | 2.432 (6) |
| Nb—N2 | 2.021 (4) | Nb—C5 | 2.424 (5) |
| Nb—C1 | 2.405 (6) | | |
| Cl1—Nb2—Cl2 | 78.78 (5) | Cl2—Nb2—N1 | 83.5 (1) |
| Cl1—Nb2—N1 | 140.4 (1) | Cl2—Nb2—N2 | 138.2 (1) |
| Cl1—Nb2—N2 | 85.5 (1) | N1—Nb2—N2 | 84.7 (2) |

Di-*tert*-butyl-1,2-ethanediimine (0.47 g, 2.8 mmol) in 10 ml toluene was added to a solution of ($\eta^5$-Cp)NbCl$_2$(PMe$_3$)$_3$ (0.9 g, 1.9 mmol) in 50 ml toluene under argon. The reaction medium was irradiated (125 W) for 10 d during which time the red-brown colour changed to red, with formation of crystals and a precipitate. The crystals, isolated by filtration and shown by analysis to be ($\eta^5$-Cp)NbCl$_2$($^t$BuNC$_2$H$_2$N$^t$Bu) (0.5 g, 45%), were slightly soluble in dichloromethane or acetonitrile, but more soluble in nitromethane. The monocrystal was introduced, under argon, into a sealed Lindeman capillary.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71135 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1029]

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# Structure of the Dimeric Complex of Iron(III) Chloride with Pyridoxine

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## Abstract

The structure of di-$\mu$-pyridoxinato-bis[aquadichloroiron(III)], [FeCl$_2$($\mu$-C$_8$H$_{10}$NO$_3$)(H$_2$O)]$_2$, consists of centrosymmetrical dimers in which Fe atoms with a slightly distorted octahedral coordination are bridged by the O atoms of two deprotonated 4-hydroxymethyl groups of the chelating pyridoxinato anions. The other four positions of each Fe coordination octahedron are occupied by two Cl atoms, the phenolate O atom of the pyridoxinato ligand and the water molecule. The main interatomic distances are Fe—O(4-hydroxymethyl) 1.998 (2) and 1.990 (2) Å, Fe—O(phenolate) 1.949 (2) Å, Fe—Cl 2.361 (1) and 2.327 (1) Å and Fe—OH$_2$ 2.185 (2) Å.

## Comment

Pyridoxine (PN) is a vitamin of the B$_6$ group and plays an important role in the transformations of amino acids in biological systems (Robinson, 1966). The biological activity of pyridoxine is affected by its transition into the biologically active form of vitamin B$_6$ which is commonly known as pyridoxal. Metal ions have been shown to accelerate the transformation of pyridoxine to pyridoxal and their complexes with pyridoxine are used in the treatment of several diseases (Clements & Anderson, 1980; Hakimov, 1976), for example the iron(III) complex is used in

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