

## Structure of Morpholinium *trans*-Tetrachlorobis(4-methylpyridine)tungstate(III)

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(Received 1 December 1989; accepted 2 July 1990)

**Abstract.**  $C_4H_{10}NO^+[W(Cl)_4(C_6H_7N)_2]^-$ ,  $C_4H_{10}NO^+ = \text{MorphH}^+$ ,  $C_6H_7N = 4\text{-pic}$ ,  $M_r = 600.05$ , monoclinic,  $C2/c$ ,  $a = 12.156(3)$ ,  $b = 11.153(3)$ ,  $c = 35.104(5)$  Å,  $\beta = 96.38(2)^\circ$ ,  $V = 4729.8(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.685$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 5.45$  mm<sup>-1</sup>,  $F(000) = 2328$ ,  $T = 293$  K,  $R = 0.037$  for 2368 reflections. The unit cell contains *trans*- $[W(Cl)_4(4\text{-pic})_2]^-$  octahedral anions and  $\text{MorphH}^+$  in the chair conformation. The 4-methylpyridine rings are mutually staggered. Average W—Cl and W—N(4-pic) bond lengths are 2.427(2) and 2.175(14) Å.

**Introduction.** The tungsten(III) atom in *trans*- $[W(X)_4L_2]$  ( $X = \text{Cl, Br}$ ;  $L = \text{pyridine, py}$ ; 4-methylpyridine, 4-pic) can be reduced to the three-valent state by various reducing agents (Brenčič, Čeh & Leban, 1986, 1987). All products of reduction contain *trans*- $[W(X)_4L_2]^-$ . Several compounds of this type, such as  $\text{NH}_4[W(Cl)_4(4\text{-pic})_2] \cdot 4H_2O$ , have been structurally characterized (Brenčič, Čeh & Leban, 1988). The neutral ligands of the anion are generally in the nearly ideal eclipsed conformation. The only exception found thus far is the compound (4-picH)- $[W(Cl)_4(4\text{-pic})_2] \cdot 4\text{-pic}$ , where the angle between the 4-pic planes is  $70.1^\circ$  (Brenčič, Čeh & Leban, 1987).

Compounds containing *trans*- $[W(X)_4L_2]^-$  are often solvated.  $(\text{MorphH})[W(Cl)_4(4\text{-pic})_2]$  is among the few exceptions.

**Experimental.** Morpholine (1.5 ml) was added to a solution of (4-picH) $[W(Cl)_4(4\text{-pic})_2]$  (0.6 g) in a 1:1 mixture of 2-propanol/methyl cyanide (25 ml). The solution was concentrated under vacuum. One of the red single crystals of approximate dimensions  $0.12 \times 0.16 \times 0.24$  mm was sealed under argon in a capillary.

Lattice parameters were calculated from a least-squares refinement of the  $\theta$  angles of 25 reflections ( $7 < \theta < 11^\circ$ ). The data were collected with an Enraf-Nonius CAD-4 diffractometer,  $\omega$ - $2\theta$  scans,  $\theta_{\min} = 1$ ,  $\theta_{\max} = 28^\circ$ ,  $\theta$ -scan width =  $(0.8 + 0.3 \tan \theta)^\circ$ , horizontal counter aperture =  $(2.4 + 0.9 \tan \theta)$  mm, variable scan rate, maximum scan rate time = 40 s. 3958 independent reflections ( $-14 \leq h \leq 14$ ,  $0 \leq k \leq 14$ ,  $0 \leq l \leq 42$ ) were measured, 2368 with  $I > 3\sigma(I)$  were used for the solution and refinement of the structure.

Three standard reflections  $\bar{2}29$ ,  $\bar{3}37$ ,  $\bar{3}33$  showed no decay during data collection and no reorientation of the crystal was necessary.

Structure factors were corrected for Lp effects but not for absorption. The W atom was located from the Patterson map. Fourier syntheses and least-squares refinement gave the positions of the rest of the non-H atoms. H atoms in calculated positions were included with an assumed  $U_{\text{iso}} = 0.11$  Å<sup>2</sup>. Anisotropic refinement on  $F$  for all non-H atoms ended with  $R = 0.037$  and  $wR = 0.04$ ,  $w = 1.0/[\sigma^2(F) + 0.0037F^2]$ . The programs *SHELX76* (Sheldrick, 1976), *GEOM* (Mallison & Muir, 1985) and *ORTEP* (Johnson, 1965) were used. The maximum shift-to-e.s.d. ratio in the last cycle was 0.2. Final difference Fourier synthesis had a maximum located at  $x = 0.25$ ,  $y = 0.25$ ,  $z = 0.5$  with  $\Delta\rho = 2.2$  e Å<sup>-3</sup>. Minimum  $\Delta\rho = -1.2$  e Å<sup>-3</sup>.

All calculations were carried out on CDC Cyber-172 computer. Atomic scattering factors for neutral atoms from Cromer & Mann (1968) and the anomalous-dispersion corrections of Cromer (1965) were applied. Scattering factors for H atoms were from Stewart, Davidson & Simpson (1965). The positional and equivalent isotropic thermal parameters are listed in Table 1\* and bond distances and angles in Table 2. The numbering scheme of the cation and anion is shown in Fig. 1. A stereoscopic projection of the unit cell is shown in Fig. 2.

**Discussion.** The unit cell contains eight cations and anions in general positions. The 4-methylpyridine ligands of the cation are mutually *trans*. The planes of the aromatic rings are in the staggered conformation. Thus, the angle between these planes is  $89.9(1)^\circ$ , they make angles of  $88.0$  and  $91.9^\circ$  with the basal  $WCl_4$  plane and cut the  $\text{Cl}(1)\cdots\text{Cl}(4)$  or  $\text{Cl}(1)\cdots\text{Cl}(3)$  vectors approximately in half. W—Cl bond lengths range from 2.415(5) to 2.437(4) Å and W—N(4-pic) distances are 2.17(2) and 2.18(2) Å. Comparable values are found in the crystal struc-

\* 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 53365 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and equivalent isotropic thermal ( $\text{\AA}^2 \times 10^3$ ) parameters with e.s.d.'s in parentheses

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$
W	0.46467 (5)	0.08919 (5)	0.12494 (2)	28
Cl(1)	0.6051 (3)	0.1341 (4)	0.0826 (1)	43
Cl(2)	0.3250 (3)	0.0350 (4)	0.1659 (1)	43
Cl(3)	0.4183 (3)	-0.0897 (4)	0.0867 (1)	44
Cl(4)	0.5177 (3)	0.2695 (4)	0.1605 (1)	45
N(1)	0.5868 (9)	-0.0093 (10)	0.1629 (3)	27
C(11)	0.6573 (11)	-0.0881 (14)	0.1498 (4)	34
C(12)	0.7350 (15)	-0.1467 (16)	0.1722 (5)	50
C(13)	0.7450 (13)	-0.1303 (14)	0.2122 (5)	43
C(14)	0.6702 (13)	-0.0504 (15)	0.2272 (5)	42
C(15)	0.5932 (11)	0.0091 (12)	0.2007 (4)	30
C(16)	0.8344 (15)	-0.1969 (17)	0.2384 (6)	63
N(2)	0.3431 (9)	0.1898 (11)	0.0877 (4)	37
C(21)	0.2405 (13)	0.1487 (16)	0.0773 (5)	49
C(22)	0.1626 (14)	0.2096 (17)	0.0519 (5)	55
C(23)	0.1892 (16)	0.3193 (18)	0.0379 (5)	60
C(24)	0.2922 (16)	0.3620 (16)	0.0485 (5)	52
C(25)	0.3672 (15)	0.2995 (15)	0.0728 (5)	49
C(26)	0.1041 (16)	0.3881 (17)	0.0109 (5)	61
N(31)	0.1785 (12)	0.2048 (14)	0.3660 (4)	54
C(32)	0.1131 (17)	0.1086 (17)	0.3787 (6)	63
C(33)	-0.0013 (21)	0.1125 (20)	0.3593 (6)	79
O	-0.0037 (17)	0.1056 (17)	0.3173 (8)	146
C(35)	0.0708 (16)	0.2093 (18)	0.3032 (6)	69
C(36)	0.1814 (14)	0.2028 (17)	0.3261 (6)	58

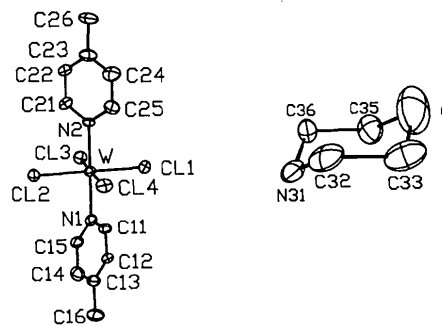


Fig. 1. Numbering schemes of the anion and cation.

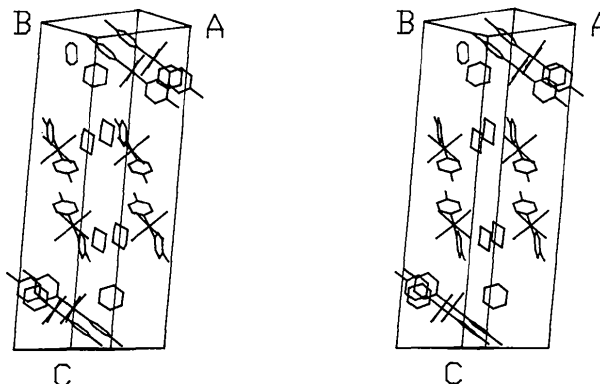


Fig. 2. Stereoscopic projection of the unit cell.

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

W—Cl(1)	2.437 (4)	N(2)—C(21)	1.34 (2)
W—Cl(2)	2.421 (4)	C(21)—C(22)	1.40 (3)
W—Cl(3)	2.436 (5)	C(22)—C(23)	1.37 (3)
W—Cl(4)	2.415 (5)	C(23)—C(24)	1.35 (3)
W—N(1)	2.18 (2)	C(24)—C(25)	1.37 (3)
W—N(2)	2.17 (2)	C(25)—N(2)	1.37 (3)
N(1)—C(11)	1.34 (2)	C(23)—C(26)	1.53 (3)
C(11)—C(12)	1.33 (3)	N(31)—C(32)	1.44 (3)
C(12)—C(13)	1.41 (3)	C(32)—C(33)	1.48 (4)
C(13)—C(14)	1.42 (3)	C(33)—O	1.47 (4)
C(14)—C(15)	1.41 (3)	O—C(35)	1.58 (3)
C(15)—N(1)	1.34 (2)	C(35)—C(36)	1.49 (3)
C(13)—C(16)	1.54 (3)	C(36)—N(31)	1.40 (3)
Cl(1)—W—Cl(4)	88.8 (2)	N(2)—W—Cl(1)	90.1 (4)
Cl(1)—W—Cl(2)	177.3 (2)	N(2)—W—Cl(4)	90.3 (4)
Cl(4)—W—Cl(2)	93.7 (2)	N(2)—W—Cl(2)	90.7 (4)
Cl(4)—W—Cl(3)	176.9 (2)	N(2)—W—Cl(3)	89.5 (4)
Cl(2)—W—Cl(3)	89.4 (2)	N(1)—C(11)—C(12)	123.8 (1)
Cl(3)—W—Cl(1)	88.1 (2)	C(11)—C(12)—C(13)	120.2 (2)
N(1)—W—Cl(1)	90.0 (3)	C(12)—C(13)—C(16)	120.9 (2)
N(1)—W—Cl(4)	88.8 (4)	C(12)—C(13)—C(14)	117.7 (2)
N(1)—W—Cl(2)	89.2 (3)	C(13)—C(14)—C(15)	117.2 (2)
N(1)—W—Cl(3)	91.4 (4)	C(14)—C(13)—C(16)	121.4 (2)
N(1)—W—N(2)	179.1 (5)	C(14)—C(15)—N(1)	123.1 (1)
N(2)—C(21)—C(22)	123.3 (2)	C(15)—N(1)—C(11)	118.0 (1)
C(21)—C(22)—C(23)	119.4 (2)	N(31)—C(32)—C(33)	111.1 (2)
C(22)—C(23)—C(26)	120.0 (2)	C(32)—C(33)—O	111.8 (2)
C(22)—C(23)—C(24)	117.7 (2)	C(33)—O—C(35)	109.1 (2)
C(23)—C(24)—C(25)	121.6 (2)	O—C(35)—C(36)	108.0 (2)
C(24)—C(23)—C(26)	122.3 (2)	C(35)—C(36)—N(31)	114.6 (2)
C(24)—C(25)—N(2)	122.4 (2)	C(36)—N(31)—C(32)	111.9 (2)
C(25)—N(2)—C(21)	115.5 (1)		

tures of (4-picH)[W(Cl)<sub>4</sub>(4-pic)<sub>2</sub>].4-pic (Brenčič, Čeh & Leban, 1987) and NH<sub>4</sub>[W(Cl)<sub>4</sub>(4-pic)<sub>2</sub>].4H<sub>2</sub>O (Brenčič, Čeh & Leban, 1988).

The 4-methylpyridine rings are planar to within 0.01  $\text{\AA}$ . Average C—C, C—N and C—CH<sub>3</sub> bonds are 1.38, 1.35 and 1.54  $\text{\AA}$ . All *cis* octahedral angles are close to 90°.

The morpholinium ion is in the chair conformation. Average C—C, C—O and C—N bonds are 1.48, 1.53 and 1.42  $\text{\AA}$ . The central C atoms are coplanar to within 0.01  $\text{\AA}$ . The angle between the planes defined by the atoms O, C(33), C(35) and N(31), C(32), C(36) is 1.9°. All ring angles are around 110°. N(31) is 0.62  $\text{\AA}$  on one side and O 0.67  $\text{\AA}$  on the other side of the plane of the four central C atoms.

Cations and anions are also connected by two weak hydrogen bonds between Cl(1)⋯N(31)( $-x, y, \frac{1}{2} + z$ ) 3.12 (1)  $\text{\AA}$  and Cl(3)⋯N(31)( $\frac{1}{2} + x, \frac{1}{2} + y, z$ ) 3.14 (2)  $\text{\AA}$ . The sum of the van der Waals radii of N and Cl atoms is from 3.25 to 3.45  $\text{\AA}$  (Huheey, 1983).

We are indebted to the University Edvard Kardelj of Ljubljana and the Research Community of Slovenia for support.

#### References

- BRENCIČ, J. V., ČEH, B. & LEBAN, I. (1986). *Z. Anorg. Allg. Chem.* **538**, 212–220.

- BRENČIČ, J. V., ČEH, B. & LEBAN, I. (1987). *Z. Anorg. Allg. Chem.* **549**, 233–239.  
 BRENČIČ, J. V., ČEH, B. & LEBAN, I. (1988). *J. Cryst. Spectrosc. Res.* **18**, 345–351.  
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 HUHEEY, J. E. (1983). *Inorganic Chemistry: Principles of Structure and Reactivity*, p. 258. Cambridge: Harper.

- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL 3794. Oak Ridge National Laboratory, Tennessee, USA.  
 MALLISON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

*Acta Cryst.* (1991). **C47**, 313–315

## Structure of *trans*-(Ethanenitrile)(hydrido)bis(tricyclohexylphosphine)platinum Tetraphenylborate Dichloromethane Solvate

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(Received 7 August 1989; accepted 17 July 1990)

**Abstract.** *trans*-[Pt(H){P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>N)][B-(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>].CH<sub>2</sub>Cl<sub>2</sub>, *M<sub>r</sub>* = 1202.1, triclinic, *P* $\bar{1}$ , *a* = 11.462 (4), *b* = 14.274 (5), *c* = 19.715 (8) Å,  $\alpha$  = 74.89 (3),  $\beta$  = 78.24 (3),  $\gamma$  = 85.54 (3)°, *V* = 3048 (2) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.31 g cm<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71073 Å,  $\mu$  = 25.0 cm<sup>-1</sup>, *T* = 296 K, *F*(000) = 1248, *R* = 0.0411 for 6847 observed reflections [*I* > 3 $\sigma$ (*I*)]. The cation has a distorted square-planar geometry, with Pt—P 2.302 (2) and Pt—N 2.079 (6) Å. The P—Pt—P angle is 161.4 (1)°.

**Introduction.** There is continuing interest in the steric demands of bulky ligands and the distortions they undergo to relieve strain in overcrowded systems. In particular, Pt complexes containing the bulky ligand PCy<sub>3</sub> (Cy = cyclohexyl, C<sub>6</sub>H<sub>11</sub>) have been the subject of a recent review (Clark & Hampden-Smith, 1987). Distortions of complexes *trans*-Pt(PCy<sub>3</sub>)<sub>2</sub>H*X* from an ideal square-planar geometry, which occur to accommodate the bulky phosphine ligands, depend to some degree on the size of the substituent *X*. In this paper, we report the effects of the ligand NCCH<sub>3</sub> on distortions in *trans*-[Pt(H)(PCy<sub>3</sub>)<sub>2</sub>(NCCH<sub>3</sub>)] [BPh<sub>4</sub>].

**Experimental.** The compound was prepared by reaction of *trans*-Pt(PCy<sub>3</sub>)<sub>2</sub>H(SiPh<sub>2</sub>OSO<sub>2</sub>CF<sub>3</sub>) with NaBPh<sub>4</sub> and acetonitrile in dichloromethane. Crystals were grown by slow cooling of a concentrated dichloromethane solution layered with pentane. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  18.46 (*t*, <sup>2</sup>*J*<sub>H—P</sub> = 12 Hz, <sup>1</sup>*J*<sub>H—Pt</sub> = 1234 Hz, 1 H), 1.0–2.2 (*m*, 69 H), 6.87 (*t*, <sup>3</sup>*J*<sub>H—H</sub> = 7 Hz, 4 H), 7.03 (*t*, <sup>3</sup>*J*<sub>H—H</sub> = 7 Hz, 8 H), 7.73 (*br s*, 8 H). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  40.66 (<sup>1</sup>*J*<sub>Pt—P</sub> =

2677 Hz). (Proton chemical shifts are relative to Me<sub>4</sub>Si at 0.00 p.p.m.; phosphorus chemical shifts are relative to 85% H<sub>3</sub>PO<sub>4</sub> at 0.00 p.p.m.)

A colorless crystal exhibiting an irregular shape and dimensions of 0.34 × 0.42 × 0.50 mm was mounted in a thin-walled glass capillary and flame sealed. Data were measured with a Siemens *R3m/V* diffractometer equipped with a highly oriented graphite monochromator set for Mo *K* $\alpha$  radiation. Orientation matrix and unit-cell parameters were obtained from 23 randomly selected reflections with 15 ≤ 2 $\theta$  ≤ 30°. Intensities were measured using  $\omega$ -2 $\theta$  scans (3 ≤ 2 $\theta$  ≤ 50°) at a variable scan speed, 5.0–29.3° min<sup>-1</sup> in 2 $\theta$ , *hkl* ranges -13 < *h* < 13, -17 < *k* < 17, -1 < *l* < 23. A total of 12 496 reflections were measured, of which 10 747 were unique (*R*<sub>int</sub> = 3.3 %). Three check reflections (161, 517, 1.2.11) revealed a linear decay to 81% of the initial intensity data collection. The data were corrected for this decay, as well as for Lorentz and polarization effects, and for absorption. The absorption correction was made using the  $\psi$ -scan method, based on eight reflections with 5 ≤ 2 $\theta$  ≤ 35°, with  $\chi$  in the range 260–280°. The min./max. corrections were 0.746/0.991.

The structure was solved by direct methods in *P* $\bar{1}$  and refined in *P* $\bar{1}$  by full-matrix least squares using 6847 observed reflections [*I* > 3 $\sigma$ (*I*)]. The quantity minimized was  $\sum w(F_o - F_c)^2$ , where  $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ ; *g* = 0.0006. All non-H atoms were refined anisotropically. The phenyl groups of the anion were refined as rigid hexagons [*d*(C—C) = 1.40 Å]. All H atoms, except for H(Pt), were placed in calculated, idealized positions [*d*(C—H) = 0.96 Å, isotropic thermal parameters approximately equal to 1.2 times the

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