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## Structure of Acetamidine(bromo)bis( $\eta^5$ -cyclopentadienyl)tungsten(IV) Hexafluorophosphate, $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}(\text{C}_2\text{H}_6\text{N}_2)][\text{PF}_6]$

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**Abstract.**  $\text{C}_{12}\text{H}_{16}\text{BrN}_2\text{W}^+\cdot\text{F}_6\text{P}^-$ ,  $M_r = 596.9$ , orthorhombic,  $Pbcm$ ,  $a = 7.2879$  (9),  $b = 13.563$  (2),  $c = 16.661$  (2) Å,  $V = 1646.9$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.40$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 96.62$  cm<sup>-1</sup>,  $F(000) = 1120$ , room temperature,  $R = 0.042$  for 1572 observed reflections with  $F_o \geq 3\sigma F_o$ . The  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}(\text{HNCCH}_3\text{NH}_2)]^+$  cation is disordered in  $Pbcm$ . The W atom is coordinated by two  $\eta^5$ -cyclopentadienyl rings (Cp), a Br and one of the N atoms of the acetamidine ligand, in a distorted tetrahedral environment. The W atom is 1.977 (1) and 2.013 (1) Å from the least-squares planes defined by the cyclopentadienyl rings with higher probability. These rings adopt an eclipsed orientation and the angle Cp—W—Cp between ring normals is 130 (1)°. The W—Br and W—N bond lengths are 2.580 (6) and 2.21 (2) Å and the angle N—W—Br is 75.5 (6)°.

**Experimental.** The crystals of the title complex were prepared by C. Romão, Centro de Química Estrutural (Calhorda, Carrondo, Dias, Domingos, Duarte, Garcia & Romão, 1987). Unit-cell parameters refined from 25 centred reflections in the range  $15 < \theta < 18^\circ$ . Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation. 2744  $hkl$  intensities were measured using  $\omega$ - $2\theta$  scan mode, with  $1.5 \leq \theta \leq 30^\circ$  for one octant of the reflection sphere  $h$  from 0 to 10,  $k$  from 0 to 18 and  $l$  from 0 to 23. Two standard reflections 438 and 0,10,3 monitored every 3600 s and their intensities showed no decay throughout data collection. Intensity data corrected for Lorentz and polarization effects with CAD-4 software and empirically for absorption (North, Phillips & Mathews, 1968) (transmission factors

between 0.461 and 0.999). 1572 reflections with  $F_o \geq 3\sigma F_o$  were used in the solution and refinement of the structure. The W-atom position was found from a sharpened Patterson synthesis map and non-H-atom positions were located from subsequent difference Fourier syntheses. The Laue symmetry and systematic absences observed were consistent with space groups  $Pbcm$  and  $Pbc2_1$ . Initially, in agreement with crystal-density calculations, the refinement with isotropic temperature factors for non-H atoms was made in the noncentrosymmetric space group. However, the highest peaks around the metal atom could only be explained if a disordered model was considered in space group  $Pbcm$ . In this space group the unit cell contains four  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{Br}(\text{HNCCH}_3\text{NH}_2)]^+$  cations and four  $[\text{PF}_6]^-$  anions. In the asymmetric unit, the W and one C of each Cp ring lies on a mirror plane, while the P and two F atoms are on a twofold axis. Thus, the two equatorial ligands, Br and acetamidine have 50% probability of being on each side of that mirror plane. Furthermore, the Cp rings are also disordered with a higher probability orientation of 57 (4) for Cp<sub>1</sub> and 71 (4)% for Cp<sub>2</sub>) and a second orientation with 43 (4) for Cp<sub>1</sub> and 29 (4)% for Cp<sub>2</sub> as refined occupancies, respectively. The two orientations with higher occupancies on each side of the W atom adopt an eclipsed configuration for the Cp rings, while any other combination between these and the orientations with lower occupancy of the rings results in a staggered arrangement. The isotropic refinement of this model gave a value of  $R = 0.072$ . The final refinements (on  $F$  with unit weights), with anisotropic temperature factors for W, P, F and the atoms of the acetamidine

ligand, isotropic temperature factors for the C atoms of the Cp rings with C—C distances restrained to 1.40 Å, reduced *R* to 0.042. The H atoms were not included in the final model. In the final cycle, the maximum shift/e.s.d. was 0.127 on refined atomic coordinates. In the final difference map the magnitudes of the remaining peaks were in the range  $-1.54$  to  $0.85$  e Å<sup>-3</sup>. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Solution and refinement of the structure were carried out with *SHELX76* (Sheldrick, 1976). Drawings were made with *ORTEPII* (Johnson, 1976). Fig. 1 shows the molecular structure of the cation with one of the 50% probability positions for the Br and acetamidine ligands, and the two higher probability orientations for the Cp rings. Table 1 gives final atomic parameters.\* Table 2 gives selected bond lengths and angles for the complex.

**Related literature.** The W—N bond length is slightly longer than the values registered for the complex [W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Br(H<sub>2</sub>NNC<sub>6</sub>H<sub>5</sub>)] [BF<sub>4</sub>], (Cowie & Gauthier, 1980), 2.156 (9) and 2.034 (9) Å. The W—Br bond lengths are also longer than the W—Br bond lengths observed in other organometallic complexes [ReW<sub>2</sub>(μ-Br)(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)-(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)-(μ-CO)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 2.511 (2) Å and [ReW<sub>2</sub>(μ-Br)(μ-O)-(μ-CC<sub>6</sub>H<sub>4</sub>Me-4)-(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] 2.515 (3) Å (Carriedo, Jeffrey & Stone, 1984). The bond angle Br—W—N lies within

\* 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 54311 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

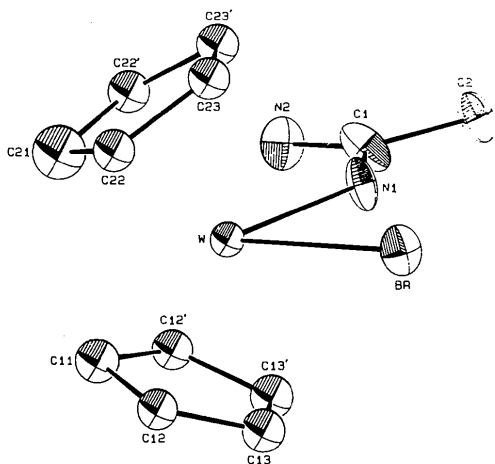


Fig. 1. Molecular structure of the title complex cation with thermal ellipsoids at the 30% probability level.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent or isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

Cp<sub>1</sub> is formed by C11, C12, C13 and C111, C121, C131 with refined occupancies of 57 (4) and 43 (4)% respectively. Cp<sub>2</sub> is formed by C21, C22, C23 and C212, C222, C232 with refined occupancies of 71 (4) and 29 (4)% respectively.

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

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
W	-1762 (1)	5770.2 (4)	2500	32.3 (1)
Br	723 (4)	4800 (2)	1730 (2)	48.6 (8)
N(1)	-77 (30)	5080 (15)	3449 (10)	40 (6)
C(1)	-176 (40)	5075 (16)	4270 (12)	53 (8)
N(2)	-1347 (27)	5567 (14)	4670 (10)	51 (6)
C(2)	1290 (33)	4494 (16)	4690 (12)	47 (7)
C(11)	-2658 (34)	7352 (20)	2500	47 (8)
C(12)	-1548 (26)	7207 (14)	1775 (10)	39 (6)
C(13)	242 (25)	7029 (15)	2080 (11)	43 (6)
C(111)	541 (60)	6994 (35)	2500	50 (14)
C(121)	-556 (39)	7151 (22)	3187 (15)	53 (9)
C(131)	-2313 (35)	7411 (22)	2937 (13)	49 (9)
C(21)	-4936 (46)	5789 (24)	2500	79 (11)
C(22)	-4314 (26)	5274 (13)	1790 (10)	52 (5)
C(23)	-3438 (26)	4378 (12)	2072 (10)	56 (6)
C(212)	-3291 (71)	4229 (35)	2500	36 (14)
C(222)	-3801 (55)	4770 (26)	1803 (19)	48 (13)
C(232)	-4787 (45)	5585 (21)	2063 (14)	31 (11)
P	3980 (6)	7500	0	48 (1)
F(1)	4001 (18)	7411 (9)	943 (5)	135 (6)
F(2)	4039 (29)	6387 (8)	-18 (9)	208 (11)
F(3)	6073 (23)	7500	0	178 (12)
F(4)	1944 (22)	7500	0	285 (19)

Table 2. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

W—Br	2.580 (6)	N(1)—C(1)	1.37 (3)
W—N(1)	2.21 (2)	C(1)—N(2)	1.27 (3)
C(1)—C(2)	1.50 (3)	F(2)—P	1.51 (1)
F(1)—P	1.58 (1)	F(4)—P	1.48 (2)
F(3)—P	1.52 (2)	W—Cp <sub>2</sub> *	2.013 (1)
W—Cp <sub>1</sub> *	1.977 (1)		
N(1)—W(1)—Br	75.5 (6)	C(1)—N(1)—W(1)	133 (2)
N(2)—C(1)—N(1)	124 (2)	C(2)—C(1)—N(1)	116 (2)
C(2)—C(1)—N(2)	121 (2)	F(2)—P—F(1)	86.7 (8)
F(3)—P—F(1)	89.4 (6)	F(3)—P—F(2)	88.4 (9)
F(4)—P—F(1)	90.6 (6)	F(4)—P—F(2)	91.6 (9)
F(4)—P—F(3)	180.0	F(1)—P—F(1)	178.9 (5)
F(2)—P—F(2)	177 (2)	Cp <sub>1</sub> —W—Cp <sub>2</sub>	130 (1)

\* These are the ring normals from the W atom to the Cp rings of higher probability.

the observed experimental range for similar complexes with two monodentate ligands (Azevedo, Calhorda, Carrondo, Dias, Félix & Romão, 1990; Carrondo, Dias, Garcia, Matias, Robalo, Green, Higgins & Yang, 1990). Bond lengths and bond angles in the complexed acetamidine in the present structure are comparable to the values found in the free molecule (Norrestam, Mertz & Crossland, 1983).

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## Bis(pyridine)[bis(salicylidene)-1,3-diaminopropanato]manganese(III) Perchlorate\*

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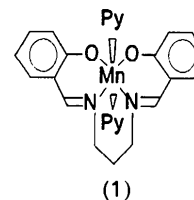
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**Abstract.**  $[\text{Mn}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)(\text{C}_{10}\text{H}_{10}\text{N}_2)](\text{ClO}_4)$ ,  $M_r = 592.9$ , orthorhombic,  $P2_12_12_1$ ,  $a = 12.596(6)$ ,  $b = 13.836(7)$ ,  $c = 15.848(8)$  Å,  $V = 2761.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.426$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.061$  mm<sup>-1</sup>,  $F(000) = 1224$ ,  $T = 293$  K,  $R = 0.057$  for 1440 unique reflexions [ $I \geq 2\sigma(I)$ ]. The manganese environment is approximately octahedral, comprising a square-planar arrangement of oxygen and nitrogen from the Schiff base, capped by pyridine. Non-bonded interactions are minimized by staggering the pyridine rings relative to the manganese—Schiff-base bonds, O—Mn—N—C  $-42.9(7)$ ,  $-63.2(6)^\circ$  and by the long pyridine Mn—N bonds of 2.307(7) and 2.388(7) Å.

**Experimental.** The complex aqua[*N,N'*-(1,3-propanediyl)bis(salicylideneaminato)]manganese(III) perchlorate dihydrate was prepared as previously described (Ashmawy, McAuliffe, Parish & Tames, 1985). To a solution of this complex (0.5 g) in methanol (200 ml) 2.0 g pyridine was added with stirring.

\* Alternative name: [*N,N'*-(1,3-propanediyl)bis(salicylideneaminato)]bis(pyridine)manganese(III) perchlorate.

On standing in the refrigerator for 5 d small black crystals of the perchlorate salt of (1) were deposited. These were separated by filtration, washed with cold methanol (3 × 25 ml) and dried over P<sub>2</sub>O<sub>5</sub>.



Crystal size 0.4 × 0.2 × 0.2 mm, Nicolet *R3m/V* diffractometer, graphite-monochromated Mo *K*α radiation, unit-cell dimensions from setting angles of 25 accurately centred reflexions ( $8.4 \leq \theta \leq 14.2^\circ$ ),  $\omega$ -2 $\theta$  scan mode,  $\omega$ -scan width 0.6° below  $K\alpha_1$  and 0.6° above  $K\alpha_2$  and scan speed ranging from 2 to 5° min<sup>-1</sup> according to the intensity gathered in a pre-scan,  $0 \leq h \leq 10$ ,  $0 \leq k \leq 15$ ,  $0 \leq l \leq 17$ ,  $0 \leq \theta \leq 25^\circ$ . 2240 unique reflexions measured, 1440 observed [ $I \geq 2\sigma(I)$ ], intensity standards ( $\bar{1}2\bar{3}$ ,  $4\bar{2}2$ ,  $30\bar{6}$ ) measured every 200 reflexions, no systematic drift,