

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

$$B_{eq} = (4/3) \sum \sum \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Cu(1)	0	0	0	2.12 (2)
Ni(1)	5000	5000	5000	1.96 (2)
N(1)	-898 (5)	-2645 (5)	526 (4)	2.67 (9)
N(2)	-1604 (5)	923 (5)	2057 (4)	2.81 (10)
N(3)	3520 (6)	1081 (5)	2048 (5)	3.38 (10)
N(4)	1617 (6)	6152 (6)	3252 (5)	3.85 (13)
C(1)	-2698 (7)	-2654 (7)	1622 (6)	3.67 (13)
C(2)	-2139 (8)	-607 (7)	2975 (6)	3.85 (15)
C(3)	4101 (6)	2539 (6)	3188 (5)	2.51 (11)
C(4)	2882 (6)	5754 (6)	3960 (5)	2.65 (12)

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

Cu(1)—N(1)	1.997 (3)	Ni(1)—C(3)	1.850 (4)
Cu(1)—N(2)	2.001 (3)	Ni(1)—C(4)	1.864 (4)
N(1)—C(1)	1.465 (6)	C(3)—N(3)	1.123 (5)
C(1)—C(2)	1.487 (7)	C(4)—N(4)	1.125 (6)
C(2)—N(2)	1.455 (6)		
N(1)—Cu(1)—N(2)	84.6 (1)	N(2)—C(2)—C(1)	108.7 (4)
Cu(1)—N(1)—C(1)	107.9 (3)	C(3)—Ni(1)—C(4)	88.1 (2)
Cu(1)—N(2)—C(2)	108.7 (3)	Ni(1)—C(3)—N(3)	177.2 (4)
N(1)—C(1)—C(2)	107.3 (4)	Ni(1)—C(4)—N(4)	176.6 (4)

distances and angles in Table 2. A stereoview of the structure and the numbering scheme is given in Fig. 1.

Related literature. Following the report (Williams, Larson & Cromer, 1972) that the mixed-valence copper cyanide ethylenediamine complex, $\text{Cu}_2(\text{CN})_4 \cdot \text{Cu}^{\text{II}}(\text{en})_2 \cdot \text{H}_2\text{O}$ (II), forms a three-dimensional network in the solid state, we attempted to prepare a

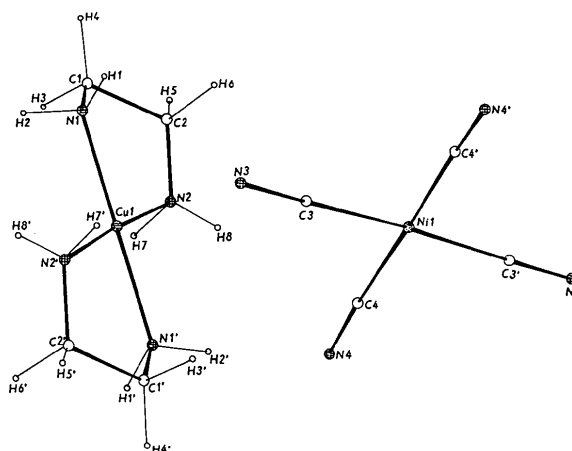


Fig. 1. A perspective view of the cation and anion and the numbering of the atoms.

C_6H_6 (or C_6D_6) clathrate of the stoichiometrically related system $\text{Ni}(\text{CN})_4\text{—Cu(en)}_2$. However, as revealed by this crystal-structure determination, the replacement of the $[\text{Cu}_2(\text{CN})_4]^{2-}$ by $[\text{Ni}^{\text{II}}(\text{CN})_4]^{2-}$ anion causes a conversion of the three-dimensional framework into a chain structure. Consequently, in contrast to (II), there is no hole formation in the present structure (I) and, as a result, no clathrate formation was observed.

References

- NRC (1973). *Crystallographic Programs for the IBM360 System*. Accession Nos. 133–147. *J. Appl. Cryst.* **6**, 309–346.
 PAVELČÍK, F. (1986). *J. Appl. Cryst.* **19**, 488–491.
 WILLIAMS, R. J., LARSON, A. C. & CROMER, D. T. (1972). *Acta Cryst.* **B28**, 858–864.

Acta Cryst. (1991). **C47**, 2448–2451

Structure of Tetracarbonyl[3,6-bis(pyridin-2-yl)-2,5-dihydro-1,2,4,5-tetrazine]-tungsten(0)

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(Received 6 November 1990; accepted 5 June 1991)

Abstract. $[\text{W}(\text{C}_{12}\text{H}_{10}\text{N}_6)(\text{CO})_4]$, $M_r = 534.14$, monoclinic, $P2_1/c$, $a = 15.327$ (2), $b = 13.993$ (2), $c =$

18.526 (2) \AA , $\beta = 114.00$ (1) $^\circ$, $V = 3629.7$ (9) \AA^3 , $Z = 8$, $D_x = 1.95$ Mg m^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71073$ \AA , $\mu = 6.535$ mm^{-1} , $F(000) = 2032$, $T = 298$ K, R (wR) = 0.023 (0.030) for 5538 unique observed reflections [I

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$> 2\sigma(I)$]. The unit cell contains two independent molecules, in each molecule the bis(pyridyl)tetrazine ligand (H_2bptz) is coordinated *via* one pyridine N and one imidic N atom of the dihydrotetrazine to the W atom at distances of 2.248 (3) and 2.209 (3) Å respectively for one molecule and 2.243 (3) and 2.205 (3) Å for the other molecule. The four carbonyl ligands are bound to tungsten with distances W—C 1.953 (5), 1.951 (4), 2.020 (6) and 2.049 (5) Å for the first molecule and 1.948 (5), 1.947 (5), 2.027 (6) and 2.023 (7) Å for the second molecule.

Experimental. Red crystals of $[W(C_{12}H_{10}N_6)(CO)_4]$ were obtained by irradiating (tungsten lamp) a solution of $[W(CO)_6]$ and H_2bptz . A rod-shaped single crystal was selected for the structure determination. Experimental data and refinement details are shown in Table 1. X-ray intensity data were collected by using graphite-monochromated Mo $K\alpha$ radiation. Cell constants were determined from setting angles of 24 reflections ($10 \leq \theta \leq 12^\circ$). Lorentz and polarization corrections were performed using local program systems. The structure was solved by using standard Patterson techniques and refined using full-matrix least-squares refinement based on F with weights $w = 1/\sigma^2(F)$. No corrections for absorption have been carried out. The non-H atoms were refined anisotropically. H atoms were placed in calculated positions and refined isotropically coupled with the adjacent C atoms. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). The programs used were written or modified by Mrs E. W. Rutten-Keulemans and Dr R. A. G. de Graaff.

Atom coordinates and equivalent isotropic thermal parameters for the non-H atoms are shown in Table 2.* Fig. 1 shows a projection of the molecule with the atomic numbering scheme; Fig. 2 depicts the unit cell in stereo projection. Relevant bond distances and angles are presented in Table 3.

Related literature. The chemistry and physical properties of metal complexes containing bridging ligands (Creutz & Taube, 1973) are generally investigated in order to measure the interaction between the mononuclear components in the ligand-bridged species across what is usually a highly conjugated ligand. We are currently interested in the synthesis of a range of novel ligand-bridged compounds (see *e.g.* Creaven, Grevels & Long, 1989; Creaven, Long,

Table 1. *Experimental data for $[W(C_{12}H_{10}N_6)(CO)_4]$*

Diffractometer	Enraf-Nonius CAD-4
Crystal dimensions (mm)	0.2 × 0.2 × 0.3
Transmission factor range	0.96–1.03
Temperature	298 K
Scan method	$\omega/2\theta$
θ range ($^\circ$)	2–30
Standard reflections	4, 7, 10, 87 $\frac{1}{2}$, 913
Number of reflections measured	10 923
Number of independent reflections	10 565
Number of observed unique reflections	5538
$[I > 2\sigma(I)]$	
R_{int}	0.046
hkl range	0 to 21, 0 to 19, –26 to 26
Number of parameters refined	567
R	0.023
wR	0.030
Weighting scheme	$1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$	0.004
S (goodness of fit)	0.89
$\Delta\rho_{max}/\Delta\rho_{min}$ ($e \text{ \AA}^{-3}$)	1.37/–0.57

Howie & McQuillan, 1989). This study was extended to systems containing 3,6-bis(pyridin-2-yl)-2,5-dihydro-1,2,4,5-tetrazine (H_2bptz), because this ligand offers the possibility of coordination as a simple chelating ligand, as a bridging chelating ligand and also as a bridging monodentate ligand. It is possible to prepare complexes of this ligand with metal carbonyl fragments under mild conditions, usually photochemically, and thus isolate thermally labile compounds which could be inaccessible by thermal routes. Tetracarbonyl[3,6-bis(pyridin-2-yl)-2,5-dihydro-1,2,4,5-tetrazine]tungsten(0) was synthesized as a preliminary investigation into the various coordination modes of this ligand. This work describes the first structural determination of a complex containing this ligand, the structural features of which may assist a more complete understanding of the excited-state properties of the related μ -[3,6-bis(pyridin-2-yl)-1,2,4,5-tetrazine]-bis[tetracarbonyltungsten(0)] compound reported previously (Kaim & Kohlmann, 1986, 1987).

The W atom appears to have an octahedral coordination. The W—CO distances of the carbon monoxide ligands *trans* to the H_2bptz N atoms are about 0.1 Å longer than the W—CO distances of the CO molecules perpendicular to the H_2bptz ligand (Table 3). This is caused by the influence of the H_2bptz ligand, which has σ -donor and π -acceptor properties different from those of the CO ligands. The observed metal–carbon and metal–nitrogen distances are similar to those reported for $M(CO)_4$ complexes containing 6-*p*-styryl-2,2'-bipyridine (Long, Vos, Howie & Kelly, 1984). The H_2bptz ligand is non-planar, which is the result of the partly saturated character of the central six-membered ring. Two H atoms are bound to N(123) and N(126) of H_2bptz . Stacking between the molecules is not observed and it is assumed that the molecules are held together by van der Waals forces. The shortest intermolecular

* Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54323 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates with *e.s.d.*'s in parentheses and isotropic thermal parameters for the non-H atoms of [W(C₁₂H₁₀N₆)(CO)₄]

$B_{eq} = (8\pi^2/3) \text{ trace } U.$				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
W(1)	0.78340 (1)	0.03369 (1)	-0.02045 (1)	2.789 (5)
W(2)	0.73259 (1)	-0.45258 (1)	0.01058 (1)	3.003 (4)
C(11)	0.7877 (3)	0.0916 (4)	0.0768 (3)	3.96 (13)
O(11)	0.7878 (3)	0.1226 (3)	0.1346 (2)	6.37 (14)
C(12)	0.9101 (3)	-0.0175 (3)	0.0429 (3)	3.41 (11)
O(12)	0.9857 (3)	-0.0454 (2)	0.0818 (2)	4.83 (10)
C(13)	0.7273 (4)	-0.0805 (4)	0.0122 (3)	4.43 (14)
O(13)	0.7014 (3)	-0.1421 (3)	0.0389 (2)	7.19 (15)
C(14)	0.8529 (4)	0.1517 (4)	-0.0361 (3)	4.25 (14)
O(14)	0.8954 (3)	0.2166 (3)	-0.0386 (3)	7.27 (15)
C(21)	0.7114 (3)	-0.3501 (4)	-0.0660 (3)	3.70 (13)
O(21)	0.6995 (3)	-0.2840 (3)	-0.1077 (2)	5.16 (11)
C(22)	0.6234 (4)	-0.5228 (4)	-0.0638 (3)	4.22 (14)
O(22)	0.5574 (3)	-0.5635 (3)	-0.1084 (2)	6.10 (13)
C(23)	0.6350 (3)	-0.3823 (4)	0.0387 (3)	4.39 (14)
O(23)	0.5742 (3)	-0.3422 (4)	0.0448 (2)	7.09 (15)
C(24)	0.8122 (4)	-0.5225 (4)	-0.0369 (3)	4.9 (2)
O(24)	0.8501 (4)	-0.5628 (3)	-0.0702 (3)	8.7 (2)
N(111)	0.6426 (3)	0.0904 (3)	-0.1074 (2)	3.24 (9)
C(112)	0.6118 (3)	0.0613 (3)	-0.1835 (2)	3.10 (11)
C(113)	0.5279 (3)	0.0952 (4)	-0.2413 (3)	4.26 (13)
C(114)	0.4743 (4)	0.1601 (4)	-0.2204 (3)	5.5 (2)
C(115)	0.5054 (4)	0.1894 (4)	-0.1434 (3)	5.6 (2)
C(116)	0.5887 (3)	0.1534 (4)	-0.0887 (3)	4.42 (14)
N(121)	0.7546 (3)	-0.0246 (2)	-0.1388 (2)	2.72 (8)
C(122)	0.6760 (3)	-0.0058 (3)	-0.1980 (2)	2.80 (10)
N(123)	0.6558 (3)	-0.0461 (2)	-0.2710 (2)	3.33 (10)
N(124)	0.6898 (3)	-0.1413 (2)	-0.2691 (2)	3.29 (10)
C(125)	0.7701 (3)	-0.1558 (3)	-0.2123 (2)	2.89 (10)
N(126)	0.8177 (3)	-0.0848 (3)	-0.1568 (2)	3.18 (9)
N(131)	0.8951 (3)	-0.2538 (3)	-0.1331 (2)	4.48 (12)
C(132)	0.8196 (3)	-0.2487 (3)	-0.2010 (3)	3.66 (13)
C(133)	0.7888 (4)	-0.3187 (4)	-0.2584 (3)	4.75 (15)
C(134)	0.8395 (5)	-0.4044 (4)	-0.2416 (4)	6.7 (2)
C(135)	0.9157 (5)	-0.4142 (4)	-0.1719 (4)	6.3 (2)
C(136)	0.9418 (5)	-0.3408 (4)	-0.1195 (4)	6.0 (2)
N(211)	0.8583 (3)	-0.3851 (3)	0.1080 (2)	3.24 (9)
C(212)	0.8931 (3)	-0.4278 (3)	0.1793 (2)	2.92 (10)
C(213)	0.9681 (3)	-0.3905 (4)	0.2436 (3)	3.54 (12)
C(214)	1.0094 (3)	-0.3065 (4)	0.2348 (3)	4.29 (14)
C(215)	0.9754 (4)	-0.2632 (4)	0.1618 (3)	4.90 (15)
C(216)	0.8996 (3)	-0.3034 (4)	0.1002 (3)	4.39 (14)
N(221)	0.7808 (3)	-0.5469 (2)	0.1149 (2)	3.17 (9)
C(222)	0.8475 (3)	-0.5198 (3)	0.1799 (2)	2.87 (10)
N(223)	0.8803 (3)	-0.5790 (2)	0.2457 (2)	3.50 (10)
N(224)	0.8106 (3)	-0.6400 (2)	0.2539 (2)	3.24 (9)
C(225)	0.7475 (3)	-0.6682 (3)	0.1884 (2)	3.11 (11)
C(226)	0.7477 (3)	-0.6405 (2)	0.1159 (2)	3.72 (11)
N(231)	0.6000 (3)	-0.7412 (3)	0.1150 (3)	5.39 (14)
C(232)	0.6728 (3)	-0.7358 (3)	0.1848 (3)	3.74 (13)
C(233)	0.6817 (5)	-0.7900 (4)	0.2497 (3)	5.6 (2)
C(234)	0.6085 (5)	-0.8534 (5)	0.2394 (4)	8.6 (3)
C(235)	0.5328 (5)	-0.8597 (6)	0.1687 (4)	9.6 (3)
C(236)	0.5306 (5)	-0.8023 (5)	0.1084 (4)	8.1 (2)

Table 3. Selected bond distances (Å) and bond angles (°) involving non-H atoms of [W(C₁₂H₁₀N₆)(CO)₄]

W(1)—C(11)	1.953 (5)	W(2)—C(21)	1.948 (5)
W(1)—C(12)	1.951 (4)	W(2)—C(22)	1.947 (5)
W(1)—C(13)	2.020 (6)	W(2)—C(23)	2.027 (6)
W(1)—C(14)	2.049 (5)	W(2)—C(24)	2.023 (7)
W(1)—N(111)	2.248 (3)	W(2)—N(211)	2.243 (3)
W(1)—N(121)	2.209 (3)	W(2)—N(221)	2.205 (3)
C(11)—O(11)	1.155 (7)	C(21)—O(21)	1.172 (6)
C(12)—O(12)	1.156 (5)	C(22)—O(22)	1.162 (6)
C(13)—O(13)	1.143 (7)	C(23)—O(23)	1.133 (8)
C(14)—O(14)	1.130 (7)	C(24)—O(24)	1.153 (9)
C(11)—W(1)—C(12)	86.9 (2)	C(21)—W(2)—C(22)	90.9 (2)
C(11)—W(1)—C(13)	84.8 (2)	C(21)—W(2)—C(23)	84.7 (2)
C(11)—W(1)—C(14)	88.4 (2)	C(21)—W(2)—C(24)	89.5 (2)
C(11)—W(1)—N(111)	100.2 (2)	C(21)—W(2)—N(211)	96.3 (2)
C(11)—W(1)—N(121)	170.9 (2)	C(21)—W(2)—N(221)	167.3 (2)
C(12)—W(1)—C(13)	88.3 (2)	C(22)—W(2)—C(23)	85.1 (2)
C(12)—W(1)—C(14)	86.2 (2)	C(22)—W(2)—C(24)	86.8 (2)
C(12)—W(1)—N(111)	172.3 (2)	C(22)—W(2)—N(211)	172.7 (2)
C(12)—W(1)—N(121)	102.1 (2)	C(22)—W(2)—N(221)	101.7 (2)
C(13)—W(1)—C(14)	171.5 (2)	C(23)—W(2)—C(24)	170.0 (2)
C(13)—W(1)—N(111)	95.3 (2)	C(23)—W(2)—N(211)	94.1 (2)
C(13)—W(1)—N(121)	93.9 (2)	C(23)—W(1)—N(221)	94.9 (2)
C(14)—W(1)—N(111)	91.0 (2)	C(24)—W(2)—N(211)	94.6 (2)
C(14)—W(1)—N(121)	93.6 (2)	C(24)—W(2)—N(221)	92.6 (2)
N(111)—W(1)—N(121)	70.9 (1)	N(211)—W(2)—N(221)	71.0 (1)
W(1)—C(11)—O(11)	177.0 (5)	W(2)—C(21)—O(21)	175.2 (4)
W(1)—C(12)—O(12)	178.0 (4)	W(2)—C(22)—O(22)	179.0 (5)
W(1)—C(13)—O(13)	172.6 (4)	W(2)—C(23)—O(23)	171.7 (4)
W(1)—C(14)—O(14)	174.6 (4)	W(2)—C(24)—O(24)	173.8 (4)
W(1)—N(111)—C(112)	117.8 (3)	W(2)—N(211)—C(212)	118.0 (3)
W(1)—N(111)—C(116)	123.9 (3)	W(2)—N(211)—C(216)	124.1 (3)
W(1)—N(121)—C(122)	120.8 (3)	W(2)—N(221)—C(222)	120.1 (3)
W(1)—N(121)—N(126)	124.9 (2)	W(2)—N(221)—N(226)	125.1 (3)

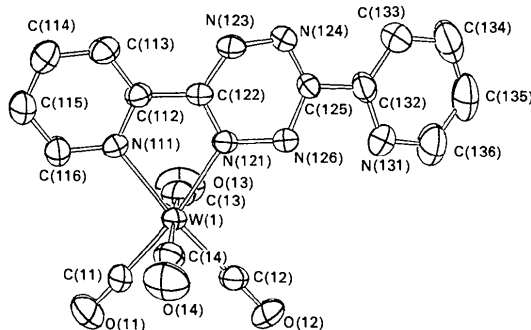


Fig. 1. Structure of [W(C₁₂H₁₀N₆)(CO)₄]. Thermal ellipsoids are shown at 50% probability. H atoms have been omitted for clarity.

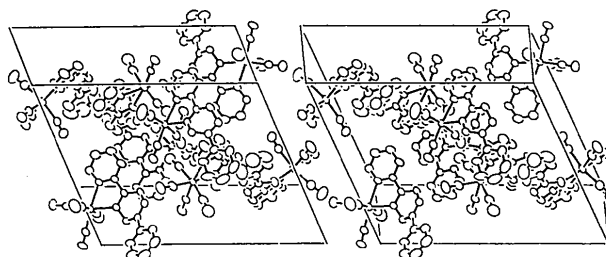


Fig. 2. Stereoscopic projection showing the packing in the unit cell. *z* is horizontal, *x* is vertical and *y* is in the plane of the paper.

distance of 2.77 Å is between H(133) and O(13) of two different molecules.

We are indebted to Mr S. Gorter, Leiden University, for collecting the X-ray data set. Professor Dr J. Reedijk and Mr J. H. van Hal are thanked for many useful discussions and for critically reading this manuscript.

References

- CREAVEN, B. S., GREVELS, F. W. & LONG, C. (1989). *Inorg. Chem.* **28**, 2231–2234.
- CREAVEN, B. S., LONG, C., HOWIE, R. A. & MCQUILLAN, G. P. (1989). *Inorg. Chim. Acta*, **157**, 151–152.
- CREUTZ, C. & TAUBE, H. (1973). *J. Am. Chem. Soc.* **95**, 1086–1094.
- HOWIE, R. A., IZQUERDO, G. & MCQUILLAN, G. P. (1983). *Inorg. Chim. Acta*, **72**, 165–172.
- KAIM, W. & KOHLMANN, S. (1986). *Inorg. Chem.* **25**, 3306–3310.
- KAIM, W. & KOHLMANN, S. (1987). *Inorg. Chem.* **26**, 68–77.
- LONG, C., VOS, J. G., HOWIE, R. A. & KELLY, J. M. (1984). *J. Organomet. Chem.* **272**, 385–390.

Acta Cryst. (1991). **C47**, 2451–2453

Structure of Acetamidine(bromo)bis(η^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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(Received 9 April 1991; accepted 31 May 1991)

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) Å³, $Z = 4$, $D_x = 2.40$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 96.62$ cm⁻¹, $F(000) = 1120$, 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 η^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 α radiation. 2744 hkl intensities were measured using ω - 2θ 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 Cp₁ and 71 (4)% for Cp₂) and a second orientation with 43 (4) for Cp₁ and 29 (4)% for Cp₂ 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