CALLIGARIS, M., NARDIN, G. & RANDACCIO, L. (1972). *Coord. Chem. Rev.* **7**, 385–403.
CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry* Vol. 9, pp. 271–383. New York: John Wiley.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
International Tables for X-ray Crystallography (1974). Vol. IV, p. 149. Birmingham: Kynoch Press.
SHKOL'NIKOVA, L. M., YUMAL', E. M., SHUGAM, E. A. & VOBLIKOVA, V. A. (1970). *Zh. Strukt. Khim.* **5**, 886–890.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1983). C**39**, 865–868

Structure of η^3-Allyl[1,2-bis(dimethylphosphino)ethane]-η^6-toluenetungsten Hexafluorophosphate, $[W(C_3H_5)(C_7H_8)(C_6H_{16}P_2)]PF_6$

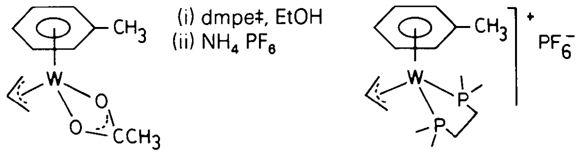
BY ANDRÉ GOURDON* AND KEITH PROUT†

Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, England

(*Received* 15 *November* 1982; *accepted* 25 *February* 1983)

Abstract. $M_r = 612{\cdot}2$, orthorhombic, $Pbc2_1$, $a = 8{\cdot}680\,(5)$, $b = 16{\cdot}230\,(4)$, $c = 30{\cdot}453\,(8)$ Å, $U = 4290$ Å^3, room temperature, $D_x = 1{\cdot}89$ Mg m^{-3} for $Z = 8$, $\mu = 5{\cdot}98$ mm^{-1}, $F(000) = 2384$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å. $R = 0{\cdot}051$ for 2273 observed reflexions. The asymmetric unit contains two crystallographically independent cations $C_{16}H_{29}P_2W^+$ together with two partially disordered PF_6^- anions. The W atoms are surrounded by a quasi planar π-toluene ligand, a π-allyl group and a chelated diphosphine ligand disordered in one of the cations.

Introduction. The crystal structure of the title compound, synthesized in accordance with the scheme below, has been determined as part of a broad study of η^6-arenetungsten complexes.



The synthesis of the starting material has been reported in a previous paper (Prout, Gourdon, Couldwell, Meunier, Miao & Woolcock, 1982).

Experimental. Small green plates of the title compound, supplied by Dr M. L. H. Green and co-workers, were very sensitive to air and moisture and were mounted for X-ray examination in argon-filled capillary tubes. It was not possible to measure their density. After survey photography by precession techniques, the selected crystal was set up on an Enraf–Nonius CAD-4F diffractometer. Cell dimensions and the orientation matrix were obtained by least squares from the setting angles of 25 reflexions. Data collection: $\sin\theta/\lambda < 0{\cdot}55$ Å^{-1}, h 0–9, k 0–17, l 0–32, $\omega/2\theta$ scans, ω-scan angle $(0{\cdot}9 + 0{\cdot}35 \tan\theta)^\circ$, graphite-monochromated Mo $K\alpha$ radiation. Reflexions with $I < 3\sigma(I)$ [$\sigma(I)$ from simple counting statistics] were omitted in subsequent calculations. Lorentz–polarization corrections and an empirical absorption correction (North, Phillips & Mathews, 1968) were applied to a set of 2277 independent observed structure amplitudes. Final weighting $w = 1/[1 + (|F_o| - 4000)^2]/3000$.

Heavy-atom techniques revealed two heavy atoms per asymmetric unit. The refinement was carried out in the non-centrosymmetric $Pbc2_1$ [$\sum w(\Delta F)^2$ minimized] with two molecules of the title compound per asymmetric unit. Subsequent F_o syntheses indicated that both PF_6^- anions and one of the dmpe ligands were partially disordered. The existence of six peaks at *ca* 1·90 Å from P(11) led us to conclude that each of the three C atoms bonded to P(11) could occupy two sites as shown in Fig. 1: C(111), C(112), C(113) and C(511), C(512) and C(513). In order to avoid ill-conditioned normal matrices, slack constraints (Waser, 1963; Rollett, 1969) were applied to both the PF_6^- anions and the dmpe group. Refinement led to occupation factors of 0·54 for C(111), C(112), C(113) and 0·46 for C(511), C(512), C(513).

For no ligand could the H atoms be found. The W and P atoms were refined anisotropically and the F and C atoms isotropically. Refinement was by least squares with a large-block approximation to the normal matrix:

---

[*] Present address: Laboratoire de Chimie des Métaux de Transition, Université P. et M. Curie, 4 place Jussieu, 75235 Paris CEDEX 05, France.

[†] To whom correspondence should be addressed.

[‡] dmpe is $(CH_3)_2P\,CH_2\,CH_2\,P(CH_3)_2$.

0108-2701/83/070865-04$01.50

one for the scale factor and the dummy overall temperature factor, one for each anion, and for each cation, one from the derivatives of the positional parameters and one from those of the corresponding temperature factors. Four of the strongest reflexions (200, 120, 122, 042) were not included in the final refinements because they were recorded at a count rate for which the dead-time error was very significant.

Final $R = 0{\cdot}051$, $R_w = 0{\cdot}052$ for 2273 reflexions. A final difference map contained no peaks greater than $0{\cdot}4\ \text{e Å}^{-3}$ except in the immediate region of the W atoms. All calculations were performed on the Oxford University ICL 2980 computer with *CRYSTALS* (Carruthers & Watkin, 1979). Scattering factors and corrections for the real part of the anomalous dispersion were from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are in Table 1,* and bond lengths and bond angles are in Table 2, together with their estimated standard deviations calculated from the variance–covariance matrix.

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$U_{eq} = (U_1U_2U_3)^{1/3}$ where U_1, U_2 and U_3 are the mean square displacements (Å^2) along each of the principal axes.

	x	y	z	U_{eq}/U_{iso}
W(1)	0·0029 (2)	0·0000	0·1859 (1)	0·0326 (5)
P(11)	0·0339 (10)	0·1057 (5)	0·1271 (3)	0·046 (5)
C(111)*	0·1899 (61)	0·0872 (43)	0·0870 (19)	0·058 (20)
C(112)*	0·0968 (79)	0·2101 (21)	0·1438 (22)	0·048 (17)
C(113)*	−0·1392 (29)	0·1183 (46)	0·0898 (11)	0·047 (15)
C(511)†	0·0700 (76)	0·0779 (40)	0·0692 (9)	0·058 (18)
C(512)†	0·1794 (57)	0·1856 (30)	0·1396 (20)	0·037 (15)
C(513)†	−0·1477 (27)	0·1716 (19)	0·1267 (18)	0·028 (13)
P(12)	−0·2575 (9)	0·0143 (6)	0·1529 (3)	0·044 (6)
C(121)	−0·4263 (42)	0·0249 (24)	0·1907 (13)	0·073 (11)
C(122)	−0·3178 (51)	−0·0603 (27)	0·1090 (15)	0·082 (13)
C(123)	−0·2815 (34)	0·1112 (16)	0·1195 (10)	0·063 (10)
C(11)	0·0230 (28)	−0·0457 (17)	0·2599 (9)	0·042 (8)
C(12)	−0·1133 (27)	0·0028 (18)	0·2530 (10)	0·040 (7)
C(13)	−0·1023 (35)	0·0856 (18)	0·2407 (12)	0·054 (10)
C(14)	0·0450 (30)	0·1179 (21)	0·2323 (10)	0·054 (8)
C(15)	0·1772 (34)	0·0659 (17)	0·2312 (11)	0·048 (9)
C(16)	0·1701 (30)	−0·0158 (17)	0·2479 (11)	0·046 (8)
C(17)	0·0209 (37)	−0·1295 (19)	0·2827 (10)	0·047 (8)
C(18)	−0·0329 (36)	−0·1337 (19)	0·1739 (9)	0·054 (9)
C(19)	0·0474 (37)	−0·952 (22)	0·1377 (10)	0·067 (11)
C(20)	0·1973 (38)	−0·0609 (24)	0·1487 (14)	0·071 (12)
W(2)	0·4746 (1)	0·1248 (1)	0·4338 (1)	0·0320 (5)
P(21)	0·5087 (13)	0·0230 (5)	0·3763 (3)	0·047 (5)
C(211)	0·6613 (51)	−0·0575 (29)	0·3797 (16)	0·045 (6)
C(212)	0·5353 (53)	0·0540 (27)	0·3186 (15)	0·094 (14)
C(213)	0·3236 (54)	−0·0470 (31)	0·3697 (16)	0·089 (15)
P(22)	0·2169 (8)	0·1132 (6)	0·4005 (3)	0·045 (6)
C(221)	0·1450 (57)	0·1925 (32)	0·3616 (17)	0·102 (17)
C(222)	0·0487 (37)	0·1162 (22)	0·4376 (11)	0·066 (9)
C(223)	0·1981 (39)	0·0125 (25)	0·3716 (12)	0·061 (10)
C(21)	0·4962 (34)	0·1920 (19)	0·5057 (11)	0·057 (9)
C(22)	0·3608 (30)	0·1417 (17)	0·4991 (10)	0·043 (8)
C(23)	0·3736 (38)	0·0542 (19)	0·4901 (12)	0·060 (10)
C(24)	0·5159 (37)	0·0122 (21)	0·4823 (11)	0·067 (10)
C(25)	0·6429 (45)	0·0687 (21)	0·4801 (14)	0·076 (13)
C(26)	0·6408 (32)	0·1535 (17)	0·4951 (11)	0·043 (9)
C(27)	0·4891 (43)	0·2746 (20)	0·5216 (10)	0·056 (9)
C(28)	0·4405 (38)	0·2583 (21)	0·4159 (10)	0·058 (10)
C(29)	0·5134 (42)	0·2185 (23)	0·3788 (11)	0·075 (11)
C(30)	0·6650 (38)	0·1997 (24)	0·3963 (13)	0·065 (11)
P(1)	1·0063 (12)	0·3541 (4)	0·0122 (3)	0·049 (6)
F(11)	0·8774 (27)	0·3298 (15)	−0·0220 (8)	0·143 (13)
F(12)	1·1024 (23)	0·3229 (13)	−0·0282 (7)	0·106 (9)
F(13)	1·1388 (28)	0·3829 (15)	0·0416 (8)	0·163 (15)
F(14)	0·9313 (29)	0·3929 (15)	0·0539 (8)	0·187 (16)
F(15)	1·0262 (25)	0·4441 (14)	−0·0023 (8)	0·140 (11)
F(16)	1·0016 (25)	0·2618 (13)	0·0259 (7)	0·128 (10)
P(2)	0·5198 (10)	0·2789 (5)	0·2366 (3)	0·055 (6)
F(21)	0·3965 (33)	0·2907 (18)	0·2727 (9)	0·387 (45)
F(22)	0·6545 (27)	0·2514 (13)	0·2667 (8)	0·114 (12)
F(23)	0·6438 (27)	0·2691 (15)	0·2021 (8)	0·159 (14)
F(24)	0·3884 (30)	0·3087 (14)	0·2053 (8)	0·162 (14)
F(25)	0·6073 (27)	0·3592 (15)	0·2245 (7)	0·149 (13)
F(26)	0·4369 (34)	0·1996 (18)	0·2477 (9)	0·352 (36)

* Site-occupation factor 0·54.

† Site-occupation factor 0·46.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Cation I		Cation II	
W(1)–P(11)	2·495 (8)	W(2)–P(21)	2·425 (8)
W(1)–P(12)	2·485 (8)	W(2)–P(22)	2·463 (7)
W(1)–C(11)	2·38 (3)	W(2)–C(21)	2·45 (4)
W(1)–C(12)	2·28 (3)	W(2)–C(22)	2·24 (3)
W(1)–C(13)	2·36 (4)	W(2)–C(23)	2·24 (4)
W(1)–C(14)	2·41 (4)	W(2)–C(24)	2·38 (4)
W(1)–C(15)	2·31 (4)	W(2)–C(25)	2·23 (5)
W(1)–C(16)	2·39 (4)	W(2)–C(26)	2·40 (4)
W(1)–C(18)	2·22 (4)	W(2)–C(28)	2·25 (4)
W(1)–C(19)	2·17 (4)	W(2)–C(29)	2·29 (4)
W(1)–C(20)	2·26 (4)	W(2)–C(30)	2·35 (4)
P(11)–C(111)	1·85 (2)	P(21)–C(211)	1·86 (5)
P(11)–C(511)	1·84 (2)		
P(11)–C(112)	1·85 (2)	P(21)–C(212)	1·84 (5)
P(11)–C(512)	1·85 (2)		
P(11)–C(113)	1·89 (2)	P(21)–C(213)	1·98 (5)
P(11)–C(513)	1·90 (2)		
P(12)–C(121)	1·87 (4)	P(22)–C(221)	1·86 (6)
P(12)–C(122)	1·88 (5)	P(22)–C(222)	1·85 (4)
P(12)–C(123)	1·88 (2)	P(22)–C(223)	1·86 (4)
C(123)–C(113)	1·54 (2)	C(223)–C(213)	1·46 (6)
C(123)–C(513)	1·54 (2)		
C(11)–C(12)	1·44 (3)	C(21)–C(22)	1·45 (3)
C(11)–C(16)	1·41 (3)	C(21)–C(26)	1·44 (3)
C(11)–C(17)	1·52 (4)	C(21)–C(27)	1·43 (5)
C(12)–C(13)	1·40 (3)	C(22)–C(23)	1·45 (4)
C(13)–C(14)	1·40 (3)	C(23)–C(24)	1·43 (4)
C(14)–C(15)	1·42 (3)	C(24)–C(25)	1·43 (4)
C(15)–C(16)	1·42 (3)	C(25)–C(26)	1·45 (4)
C(18)–C(19)	1·44 (2)	C(28)–C(29)	1·44 (2)
C(19)–C(20)	1·45 (2)	C(29)–C(30)	1·45 (2)
P(11)–W(1)–P(12)	75·1 (3)	P(21)–W(2)–P(22)	76·2 (4)
P(11)–W(1)–C(18)	124·7 (8)	P(21)–W(2)–C(28)	119·7 (8)
P(11)–W(1)–C(19)	89·2 (9)	P(21)–W(2)–C(29)	84·6 (8)
P(11)–W(1)–C(20)	82·0 (11)	P(21)–W(2)–C(30)	85·2 (10)
P(12)–W(1)–C(18)	84·2 (9)	P(22)–W(2)–C(28)	81·6 (9)
P(12)–W(1)–C(19)	87·4 (10)	P(22)–W(2)–C(29)	83·3 (10)
P(12)–W(1)–C(20)	121·2 (10)	P(22)–W(2)–C(30)	118·6 (9)
C(18)–W(1)–C(20)	66·1 (12)	C(28)–W(2)–C(30)	58 (2)
W(1)–P(11)–C(111)	116 (3)	W(2)–P(21)–C(211)	122 (2)
W(1)–P(11)–C(112)	118 (3)	W(2)–P(21)–C(212)	121 (2)
W(1)–P(11)–C(113)	115 (3)	W(2)–P(21)–C(213)	111 (2)
C(111)–P(11)–C(112)	97 (4)	C(211)–P(21)–C(212)	99 (3)
C(111)–P(11)–C(113)	102 (3)	C(211)–P(21)–C(213)	100 (2)
C(112)–P(11)–C(113)	108 (4)	C(212)–P(21)–C(213)	99 (3)
W(1)–P(11)–C(511)	122 (3)		
W(1)–P(11)–C(512)	114 (2)		
W(1)–P(11)–C(513)	108 (2)		
C(511)–P(11)–C(512)	105 (3)		
C(511)–P(11)–C(513)	106 (3)		
C(512)–P(11)–C(513)	100 (3)		

---

* Lists of structure factors, bond lengths and bond angles in the PF_6^- anions and anisotropic thermal parameters, and a partial view of cation II have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38494 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 (*cont.*)

Cation I		Cation II	
W(1)–P(12)–C(121)	118 (2)	W(2)–P(22)–C(221)	121 (2)
W(1)–P(12)–C(122)	119 (2)	W(2)–P(22)–C(222)	118 (2)
W(1)–P(12)–C(123)	113 (1)	W(2)–P(22)–C(223)	110 (2)
C(121)–P(12)–C(122)	106 (2)	C(221)–P(22)–C(222)	96 (2)
C(121)–P(12)–C(123)	100 (2)	C(221)–P(22)–C(223)	106 (3)
C(122)–P(12)–C(123)	97 (2)	C(222)–P(22)–C(223)	104 (2)
P(11)–C(113)–C(123)	106 (2)	P(21)–C(213)–C(223)	103 (4)
P(11)–C(513)–C(213)	106 (2)		
P(12)–C(123)–C(113)	107 (3)	P(22)–C(223)–C(213)	122 (3)
P(12)–C(123)–C(513)	112 (3)		
C(12)–C(11)–C(16)	121 (3)	C(22)–C(21)–C(26)	116 (3)
C(12)–C(11)–C(17)	123 (3)	C(22)–C(21)–C(27)	123 (3)
C(16)–C(11)–C(17)	116 (3)	C(26)–C(21)–C(27)	122 (3)
C(11)–C(12)–C(13)	121 (3)	C(21)–C(22)–C(23)	121 (3)
C(12)–C(13)–C(14)	118 (3)	C(22)–C(23)–C(24)	124 (4)
C(13)–C(14)–C(15)	121 (3)	C(23)–C(24)–C(25)	111 (4)
C(14)–C(15)–C(16)	121 (3)	C(24)–C(25)–C(26)	126 (4)
C(15)–C(16)–C(11)	117 (3)	C(25)–C(26)–C(21)	120 (3)
C(18)–C(19)–C(20)	115 (4)	C(28)–C(29)–C(30)	102 (3)

Angles with respect to the metal–centroid vectors [CENT(11) and CENT(12) are respectively the toluene centroid and the allyl centroid for the cation I, CENT(21) and CENT(22) the toluene centroid and the allyl centroid for the cation II]

CENT(11)–W(1)–P(11)	117·0 (8)	CENT(21)–W(2)–P(21)	123·8 (8)
CENT(11)–W(1)–P(12)	118·7 (8)	CENT(21)–W(2)–P(22)	121·2 (8)
CENT(11)–W(1)–CENT(12)	132·9 (10)	CENT(21)–W(2)–CENT(22)	129·8 (12)
CENT(12)–W(1)–P(11)	99·1 (9)	CENT(22)–W(2)–P(21)	96·3 (9)
CENT(12)–W(1)–P(12)	98·4 (9)	CENT(22)–W(2)–P(22)	94·8 (9)

The asymmetric unit contains two cations of $(\eta^3\text{-CH}_2\text{CHCH}_2)(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)(\text{dmpe})\text{W}^+$ (shown in Fig. 2) together with two PF_6^- anions. To a first approximation, the two cations are mirror images of each other. Whereas the dmpe ligand is ordered in the cation II with a puckered conformation,* this ligand is disordered in the cation I with two possible conformations, as shown in Fig. 1. The asymmetric puckered conformation found in both cations with C(513), C(123) and C(213), C(223) on the same side of the P—W—P plane as the toluene has been shown to be one of the most stable for a five-membered ring (Gollogly & Hawkins, 1971). This conformation is probably stabilized by the repulsion between the H atoms of the methyl groups of the phosphine and the H atoms of the toluene ligand. It is apparent that, due to disorder of the dmpe ligand and the PF_6^- anions, accurate structural parameters are not available and this limited accuracy precludes firm conclusions about bond lengths and bond angles.

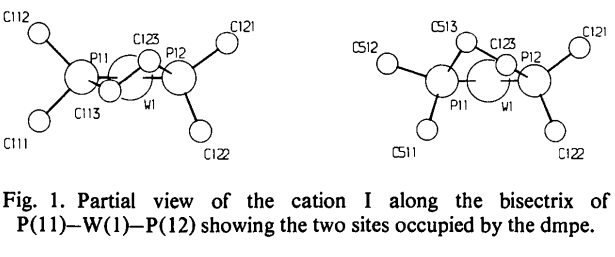


Fig. 1. Partial view of the cation I along the bisectrix of P(11)–W(1)–P(12) showing the two sites occupied by the dmpe.

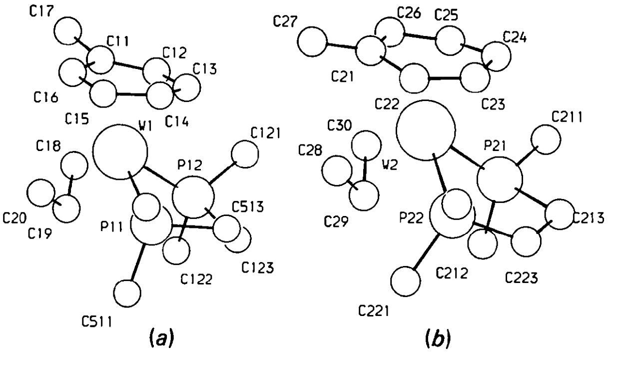


Fig. 2. The molecular structures of the cations. (*a*) Cation I. The dmpe ligand is shown in the configuration C(511), C(512), C(513). (*b*) Cation II.

The W—C(toluene) distances range from 2·23 (5) to 2·45 (4) Å, which is in agreement with previous structural studies of (η^6-toluene)tungsten complexes (Prout *et al.*, 1982). The inaccuracy of the W—C bond lengths prevents us from concluding that the pattern of variations of these bond lengths indicates that the arene shows a tendency to act as a diene, as observed in other π-arene phosphine complexes such as $\text{MoMe}_2(\eta^6\text{-C}_6\text{H}_5)(\text{PPhMe}_2)_2$ and $\text{MoMe}_2(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PPhMe}_2)_2$ (Atwood, Hunter, Rogers, Carmona-Guzman & Wilkinson, 1979). However, it is worth noting that in both cations the long W—C bonds are *trans* to the strongly π-bonding phosphine ligands. The perpendicular distances from the W atoms to the toluene rings are 1·88 (3) and 1·83 (3) Å, comparable with those found in $[\text{WH}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\{\text{P}(\text{CH}_3)_3\}_2\text{Cl}_2]^+$ [1·86 (1) Å] and $[\text{W}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)(\text{CH}_3\text{CN})_2(\eta^3\text{-CH}_2\text{CHCH}_2)]^+$ [1·83 (1) Å] (Prout *et al.*, 1982). In both cations, the perpendicular to the ring at the W atom meets the ring close to its centroid (0·03 and 0·11 Å). The W—P distances are slightly longer in the cation I than in the cation II, whereas the 'bite' angle P—W—P is smaller in I than in II allowing the same P—P separation [3·04 (2)–3·02 (2) Å].

The environment of the metal atom is very similar to that found in $[\text{W}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)(\text{CH}_3\text{CN})_2(\eta^3\text{-CH}_2\text{CHCH}_2)]^+$ with similar angles between the vectors from the benzene centroid to the metal atom and from the allyl group centroid (*ca* 130°). By comparison with Brisdon & Woolf's (1978) treatment of the $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2$ moiety, the geometry of $\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{dmpe})$ is composed of a plane defined by the P atoms and the terminal C atoms of the allyl group, which lies parallel to the arene plane at 1·12 (2) and 1·19 (2) Å from the W atom. The angle between this plane and the plane of the allyl group is *ca* 65°. The distances from the centroids of the allyl groups to the W atoms [1·94 (4) and 2·06 (4) Å] and the C—C—C angles [115 (4) and 102 (3)°] are similar to the values found in $[\text{W}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)(\text{CH}_3\text{CN})_2(\eta^3\text{-C}_3\text{H}_5)]^+$ [1·92 (3) Å and 112 (3)°].

---

* A figure illustrating this has been deposited. See deposition footnote.

References

ATWOOD, J. L., HUNTER, W. E., ROGERS, R. D., CARMONA-GUZMAN, E. & WILKINSON, G. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1519–1523.

BRISDON, B. J. & WOOLF, A. A. (1978). *J. Chem. Soc. Dalton Trans.* pp. 291–295.

CARRUTHERS, J. R. & WATKIN, D. J. (1979). *CRYSTALS User Manual*, Oxford Univ. Computing Laboratory, Oxford.

GOLLOGLY, J. R. & HAWKINS, C. J. (1971). *Inorg. Chem.* **10**, 317–322.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

PROUT, K., GOURDON, A., COULDWELL, C., MEUNIER, B., MIAO, F. M. & WOOLCOCK, J. (1982). *Acta Cryst.* B**38**, 456–462.

ROLLETT, J. S. (1969). *Crystallographic Computing*, edited by F. R. AHMED, pp. 169–172. Copenhagen: Munksgaard.

WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.

Acta Cryst. (1983). C**39**, 868–871

Structures of *N*-(4-Cyanophenyl)acetohydroxamic Acid, $C_9H_8N_2O_2$ (I), and Tris[*N*-(4-cyanophenyl)acetohydroxamato]iron(III) Hydrate, $[Fe\ (C_9H_7N_2O_2)_3].0\cdot 1H_2O$ (II)

BY RAMANA R. MOCHERLA, DOUGLAS R. POWELL, CHARLES L. BARNES AND DICK VAN DER HELM

Department of Chemistry, University of Oklahoma, Norman, OK 73019, *USA*

(*Received* 1 *December* 1982; *accepted* 3 *March* 1983)

Abstract. (I) $M_r = 176\cdot15$, orthorhombic, $Pna2_1$, $a = 7\cdot176$ (3), $b = 12\cdot549$ (2), $c = 9\cdot410$ (3) Å, $V = 847\cdot4$ Å, $Z = 4$, $D_m = 1\cdot322$, $D_x = 1\cdot341$ g cm^{-3}, $F(000) = 368$, Cu $K\bar{\alpha}$ radiation $\lambda = 1\cdot5418$ Å, $\mu = 7\cdot43$ cm^{-1}, $T = 138 \pm 2$K, $R = 0\cdot041$ for 921 data, crystals from ethyl acetate equilibrated with hexane at 277 K. (II) $M_r = 583\cdot15$, trigonal, $R\bar{3}$, $a = 13\cdot118$ (6), $c = 26\cdot728$ (19) Å, $V = 3983\cdot2$ Å^3, $Z = 6$, $D_m = 1\cdot396$, $D_x = 1\cdot422$ g cm^{-3}, $F(000) = 1782$, Mo $K\bar{\alpha}$ radiation $\lambda = 0\cdot70954$ Å, $\mu = 5\cdot69$ cm^{-1}, $T = 138 \pm 2$K, $R = 0\cdot076$ for 1839 data, crystals by evaporation from acetonitrile. In the free ligand the hydroxamate group is in a *trans* conformation. The Fe atom of the ferric complex, which lies on a crystallographic threefold axis, has a pseudo-octahedral coordination environment. Both *Λ-cis and Δ-cis* configurations of the ligand occur in the centrosymmetric crystal structure of the ferric complex.

Introduction. Hydroxamic acids, a group of weak organic acids, have wide applications as antifungal agents, food additives, inhibitors for copper corrosion in metallurgy and in nuclear fuel processing (Bauer & Exner, 1974). They form stable transition-metal complexes and therefore are used as analytical reagents (Agarwal, 1979; Agarwal & Roshania, 1980). They exhibit a high specificity for iron(III) over other biologically important metal ions, with formation constants for iron(III) as high as 10^{30}.

Under iron-limiting conditions microorganisms elaborate a variety of low-molecular-weight chelating agents (siderophores) that solubilize ferric iron in the environment and transport the iron into the cell. Many of these naturally occurring siderophores use hydroxamic acid functional groups for iron chelation and function as growth factors, antibiotics, antibiotic antagonists, tumor inhibitors, cell-division growth factors, *etc.* Some members of the ferrioxamine family of siderophores, which contain hydroxamic acid moieties, have been used as drugs for the treatment of iron overload in humans, which occurs as the result of transfusion therapy for the disease Cooley's anemia (Zaino & Roberts, 1977). There has been considerable interest in the development of synthetic and naturally occurring hydroxamic acids for use in such chelation therapy (Anderson & Hiller, 1977).

Despite widespread applications of hydroxamic acids, only few detailed structural studies have been made of transition-metal complexes of the monohydroxamic acids of the general formula *R*CON(*R'*)OH. The only X-ray diffraction study of a ferric complex of a monohydroxamic acid is that of Fe^{3+} benzohydroxamate trihydrate, which reported octahedral coordination of the Fe atom by the O atoms of the ligand (Lindner & Göttlicher, 1969). Although crystal structures of ferric complexes of several hydroxamate-type siderophores, ferrichrome (*Λ-cis*) (van der Helm, Baker, Eng-Wilmot, Hossain & Loghry, 1980), ferrichrome A (Zalkin, Forrester & Templeton, 1966), ferrichrysin (*Λ-cis*) (Norrestam, Stensland & Brändén, 1975), ferrimycobactin P (*Δ-cis*) (Hough & Rogers, 1974), tris(*N*-methylformothiohydroxamato)-iron(III) (Murray, Newman, Gatehouse & Taylor, 1978), ferric *N*,*N'*,*N''*-triacetylfusarinine (Hossain, Eng-Wilmot, Loghry & van der Helm, 1980), have been determined, so far the only crystal structures of a free ligand and its ferric complex reported are those of desferriferrioxamine E (Hossain, van der Helm &

0108-2701/83/070868-04$01.50