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Seven-coordinate thiophene-3-acetonitrile complexes of tungsten(II). Crystal structures of $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$ and $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}(AsPh_3)]$

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Abstract

Reaction of $[WI_2(CO)_3(NCMe)_2]$ with 2 equivalents of thiophene-3-acetonitrile $\{NCCH_2(3\text{-}C_4H_3S)\}$ gave the crystallographically characterised complex $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$ (**1**). The structure of **1** can be described as a distorted capped octahedron with a carbonyl group in the capping position, two carbonyl groups and an iodide in the capped face and two acetonitrile ligands and an iodide in the uncapped face. Treatment of the seven-coordinate complex $[WI_2(CO)_3(NCMe)_2]$ with an equimolar amount of L $\{L = AsPh_3$ (**2**) or PPh_3 (**3**)$\}$ followed an in situ reaction with by one equivalent of thiophene-3-acetonitrile afforded the mixed ligand complexes $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}L]$ {**2** (crystallographically characterised) and **3**}. The structure of **2** also has a capped octahedral geometry, again having a carbonyl ligand in the unique capping position. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten(II); Seven-coordinate; Thiophene-3-acetonitrile; Crystal structure

1. Introduction

Polythiophenes and their derivatives have received considerable attention over the years [1–6], mainly due to their properties as linear conducting polymers. We have previously described [7], the synthesis of the alkyne thiophene-3-acetonitrile complexes $[WI_2(CO)\{NCCH_2(3\text{-}C_4H_3S)\}(\eta^2\text{-}RC_2R)_2]$ {R = Me (crystallographically characterised) or Ph} and $[WI(CO)\{NCCH_2(3\text{-}C_4H_3S)\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$.

Hitherto, no seven-coordinate complexes of molybdenum(II) or tungsten(II) containing thiophene functionalised nitrile groups have been reported. In order to extend our work in this area we describe the synthesis and structure of the first seven-coordinate thiophene-3-acetonitrile tungsten complex $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$, and the preparation and characterisation of the new tungsten mixed ligand complexes $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}L]$ $\{L = AsPh_3$ (crystallographically characterised) and $PPh_3\}$.

2. Results and discussion

The starting material, $[WI_2(CO)_3(NCMe)_2]$ was prepared by reaction of *fac*-$[W(CO)_3(NCMe)_3]$ (prepared in situ) with an equimolar amount of I_2 at 0°C as previously reported [8]. Treatment of $[WI_2(CO)_3(NCMe)_2]$ with 2 equivalents of thiophene-3-acetonitrile in CH_2Cl_2 at r.t. gave the acetonitrile exchanged product $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$ (**1**) in 89% yield. Complex **1** has been characterised by elemental

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Table 1
Physical and analytical data for the complexes $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$ and $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}L]$ (L = $AsPh_3$ or PPh_3)

No.	Complex	Colour	Yield (%)	Analytical data (found (calcd.))		
				C	H	N
1	$[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$	Red/Brown	89	23.4 (23.4)	1.3 (1.3)	3.4 (3.6)
2	$[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}(AsPh_3)]$	Yellow	78	34.0 (34.1)	2.2 (2.1)	1.5 (1.5)
3	$[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}(PPh_3)]$	Yellow	93	35.6 (35.7)	2.3 (2.2)	1.7 (1.5)

analysis (C, H and N) (Table 1), IR (Table 2) and ^{1}H-NMR spectroscopy (Table 3), and also by X-ray crystallography. Complex **1** is very soluble in CH_2Cl_2 and moderately soluble in $CHCl_3$, but only slightly soluble in diethyl ether. The complex is air-sensitive in both the solid state and in solution, however it can be stored in the solid state under nitrogen for several days. The IR spectrum of **1** shows carbonyl bands at 2030 cm^{-1} (strong) and 1950 cm^{-1} (broad), which is typical of other bis(nitrile) complexes of the type $[MI_2(CO)_3(NCR)_2]$ [8,9]. There is also a weak nitrile band at 2291cm^{-1} and ν(C–S) bands at 1067(m) and 1024(m) cm^{-1}.

Single crystals of **1** were grown from a CH_2Cl_2/$CHCl_3$ (90:10) mixture at r.t.. The molecular structure of **1** is shown in Fig. 1, together with the atomic numbering scheme. The dimensions in the coordination sphere for **1** are given in Table 5. The metal is bonded to three carbonyl groups, two acetonitrile ligands and two iodides. The geometry of the metal environment can be considered to be a capped octahedron with one carbonyl C(100) in the capping position, two others C(200) and C(300) together with I(2) in the capped face and the two acetonitrile groups N(11), N(21) together with I(3), in the uncapped face. The bonds to the three carbonyl groups are equivalent at 1.98(1), 1.98(1), 1.99(1) Å, but the iodide in the capped face offers a longer bond {W(1)–I(2) 2.863(1) Å} than the iodide in the uncapped face {W(1)–I(3) 2.824(1) Å}. The structure is thus very similar to those found for other $[WI_2(CO)_3(NCR)_2]$ structures e.g. $[WI_2(CO)_3(NCMe)_2]$ [10], $[WI_2(CO)_3(NCEt)_2]$ [10], and $[WI_2(CO)_3(NCPh)_2]$ [11]. These also have capped octahedral structures with the iodide atoms occupying *trans* sites, one in the capped face and one in the uncapped face.

The labelling scheme for the protons of the thiophene is given in Fig. 2. The thiophene-3-acetonitrile proton resonances are shifted downfield compared to the free ligand. The ^{1}H-NMR spectrum of **1** shows three resonances in the region of 7.05–7.38 ppm due to the protons in the thiophene ring. H_a and H_b are next to a sulfur atom and therefore are shifted downfield. The signal at $\delta = 7.38$ ppm is (H_b) is a doublet of doublets with a coupling constant of $J =$ 4.98 Hz due to H_c and a coupling constant of $J =$ 3.0 Hz due to H_a. The resonance at $\delta = 7.28$ ppm can be assigned to H_a and is an apparent singlet. A doublet with $J = 2.95$ Hz would be expected because of its long range coupling to H_b. H_c is a doublet with $J = 4.89$ Hz and is coupled to H_b. The protons from the thiophene CH_2 group appear as a singlet at 4.2 ppm.

The r.t. $^{13}C\{^1H\}$-NMR spectrum ($CDCl_3$, 25°C) shows two carbonyl resonances at $\delta = 218.26$ and 200.32 ppm with an intensity ratio of 1:2. In view of

Table 2
IR data (cm^{-1})[a] for complexes **1–3**

Complex	ν(C≡N) cm^{-1}	ν(C≡O) cm^{-1}	ν(C–S) cm^{-1}
1	2291w	2030s, 1950br	1067m, 1024m
2	2288w	2035s, 1958s, 1909m	1160w, 1072w
3	2290w	2022s, 1957s, 1912m	1085m

[a] Spectra recorded in $CHCl_3$ as thin films between NaCl plates; br, broad; m, medium; s, strong; w, weak.

Table 3
^{1}H-NMR data (δ, J in Hz) for complexes **1–3**

Complex	^{1}H-NMR (δ) ppm
1	7.38 (dd, 2H_b, $J_{H-H} = 4.98$ Hz, 2.95 Hz), 7.28(2H_a, apparent singlet), 7.05(d, 2H_c, $J_{H-H} = 4.89$Hz), 4.2(s, 2H, C$\underline{H}_2$)
2	7.6–7.1 (brm, 18H, $\underline{P}h + C_4\underline{H}_3S$), 3.7(s, 2H, C$\underline{H}_2$)
3	7.6–7.1 (brm, 18H, $\underline{P}h + C_4\underline{H}_3S$), 3.7(s, 2H, C$\underline{H}_2$)

[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to $SiMe_4$.

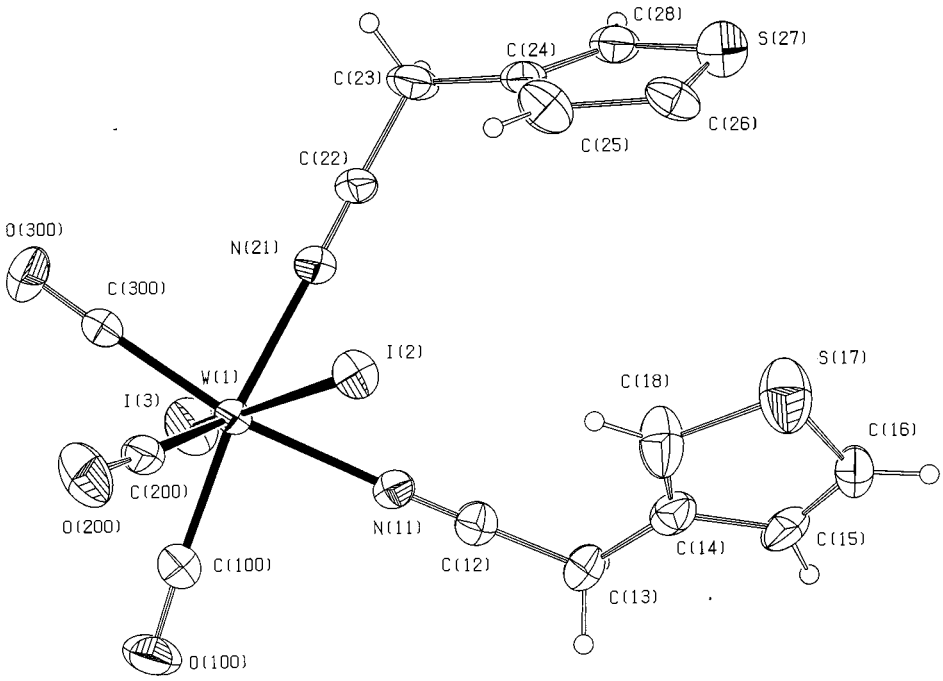

Fig. 1. The structure of $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$ (**1**), together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

Colton and Kevekordes [12] correlation of the solid state and solution state structures of seven-coordinate halocarbonyl complexes of molybdenum(II) and yungsten(II), it is likely the resonance at 218.26 is due to the unique capping carbonyl {C(100) in Fig. 1} and the resonance at 200.32 ppm can be ascribed to the equivalent octahedral carbonyl groups.

Reaction of $[WI_2(CO)_3(NCMe)_2]$ with one equivalent of L ($L = AsPh_3$ or PPh_3) in CH_2Cl_2 at r.t. gives $[WI_2(CO)_3(NCMe)L]$ [13], which when reacted in situ with an equimolar amount of thiophene-3-acetonitrile afforded the new complexes $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}L]$ (**2** and **3**) which were fully characterised (Tables 1–3). Complexes **2** and **3** are considerably less soluble than complex **1** which indicates they will be less soluble for electropolymerisation studies. They are more stable than complex **1** in both solution and the solid state.

Single crystals of **2** ($L = AsPh_3$) were grown from a $CDCl_3$ solution at room temperature. The molecular structure of **2** is shown in Fig. 3, together with the atomic numbering scheme. The dimensions in the coordination sphere for **2** are given in Table 5. The structure of **2** also shows a capped octahedral structure, but here the metal atom is bonded to three carbonyls, an acetonitrile group, the triphenylarsine ligand and two iodide ions. The capping atom is again a carbonyl group C(100) with the capped face made up of the other two carbonyl groups C(200) and C(300) and also the triphenylarsine. The uncapped face is made up of two iodide groups and the acetonitrile group. Thus in **2** the iodides are mutually *cis* while in **1** they are *trans*. Clearly, this is due to the bulk of the triphenylarsine ligand which preferentially takes up a position in the capped face. The bond lengths are W(1)–C(100) 1.90(2), W(1)–C(200), W(1)–C(300) 2.02(2), 2.00(2) Å; W(1)–As(1) 2.655(2) and W(1)–N(11) 2.204(15) with W(1)–I(3) and W(1)–I(2) 2.846(1) and 2.860(1) Å, respectively.

We are currently investigating the electropolymerisation of $[WI_2(CO)\{NCCH_2(3\text{-}C_4H_3S)\}(\eta^2\text{-}RC_2R)_2]$ ($R = Me$ or Ph) [7], and $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$ (**1**).

3. Experimental details

All reactions described in this paper were carried out under a dinitrogen atmosphere using standard Schlenk line techniques. The complex $[WI_2(CO)_3(NCMe)_2]$ [8] and $[WI_2(CO)_3(NCMe)L]$ ($L = AsPh_3$ or PPh_3) [13]

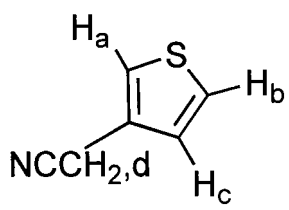

Fig. 2. ^{1}H-NMR numbering scheme for the thiophene-3-acetonitrile ligand, $NCCH_2(3\text{-}C_4H_3S)$.

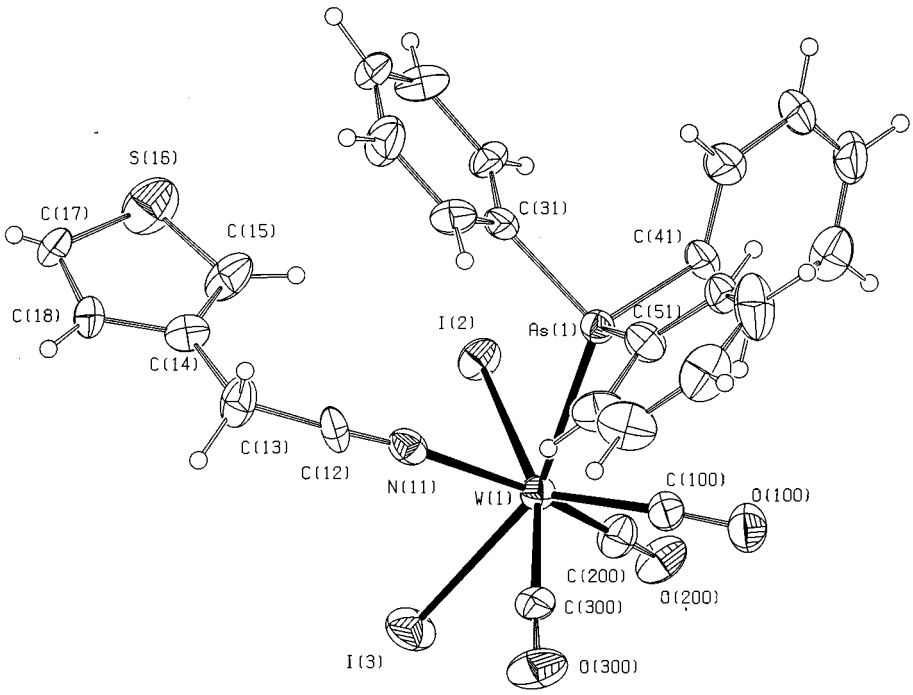

Fig. 3. The structure of $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}(AsPh_3)]$ (**2**), together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

were prepared by the literature method. All chemicals were purchased from commercial sources.

Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo–Erba Elemental Analyser MOD1108 (using helium as a carrier gas). IR spectra were recorded as thin films between NaCl plates, on a Perkin Elmer 1600 FTIR spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer (all spectra were referenced to $SiMe_4$).

3.1. $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$ (1)

To a solution of $[WI_2(CO)_3(NCMe)_2]$ (1.5 g, 1.7 mmol) in 30 cm^3 of CH_2Cl_2 was added thiophene-3-acetonitrile (0.41 g, 0.38 cm^3, 3.31 mmol). The solution was stirred in a warm water bath for 90 min and then for a further hour at r.t.. After this time the mixture was filtered and the solvent removed in vacuo to yield, the dark red-brown crystalline powder, $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}_2]$ (**1**) (yield = 1.91 g, 89%). Suitable crystals for X-ray crystallography were grown from a r.t. solution of **1** in CH_2Cl_2:$CHCl_3$ (90:10).

3.2. $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}(AsPh_3)]$ (2)

To a solution of $[WI_2(CO)_3(NCMe)_2]$ (1.5 g, 2.5 mmol) in 15 cm^3 CH_2Cl_2 was added $AsPh_3$ (0.76 g, 2.5 mmol) with continuous stirring. After 3 min the solution was filtered into a second Schlenk tube containing thiophene-3-acetonitrile (0.31 g, 0.28cm^3, 2.5 mmol) in 10 cm^3 CH_2Cl_2 and the resulting solution was stirred for 30 min. The solvent was removed in vacuo to yield, the yellow complex $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}(AsPh_3)]$ (**2**) (yield = 1.85 g, 78%). Suitable crystals for X-ray crystallography were grown from a room temperature solution of **2** in $CDCl_3$.

In a similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with 1 equivalent of PPh_3 for 1 min followed by an in situ addition of 1 equivalent of $NCCH_2(3\text{-}C_4H_3S)$ in CH_2Cl_2 affords $[WI_2(CO)_3\{NCCH_2(3\text{-}C_4H_3S)\}(PPh_3)]$ (**3**). For physical and analytical data see Table 1.

3.3. X-ray crystallography

Crystals of **1** and **2** suitable for X-ray work were prepared as described above.

3.3.1. Crystal data for 1 and 2

Crystal data and structure refinement details for **1** and **2** are given in Table 4.

3.3.2. Data collection and processing

Data for the two crystals were collected with Mo–K_α radiation using the MARresearch Image Plate System. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [14]. Both structures were solved using direct methods with the SHELX86 program [15].

Table 4
Crystal data and structure refinement for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{15}H_{10}I_2N_2O_3S_2W$	$C_{27}H_{20}AsI_2NO_3SW$
Formula weight	768.02	951.07
Temperature (K)	293 (2)	293 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
a (Å)	9.229 (9)	8.529 (8)
b (Å)	12.712 (11)	20.824 (18)
c (Å)	18.688 (18)	16.977 (17)
β (°)	105.98 (1)	102.90 (1)
Volume (Å^3)	2108	2939
Z	4	4
D_{calc} (mg mm^{-3})	2.420	2.149
Absorption coefficient (mm^{-1})	8.623	7.247
F(000)	1400	1768
Crystal size (mm)	$0.20\times0.25\times0.25$	$0.15\times0.15\times0.20$
θ range for data collection (°)	2.77–24.96	2.65–26.01
Index range	$0\le h\le10$	$0\le h\le10$
	$-15\le k\le15$	$-25\le k\le25$
	$-22\le l\le21$	$-20\le l\le20$
Reflections measured	5492	9720
Independent reflections (R_{int})	3336 (0.0332)	5451 (0.0722)
Data/restraints/parameters	3336/0/227	5451/0/327
Goodness-of-Fit on F^2	1.083	1.080
Weighting scheme (a, b)[a]	0.082, 13.755	0.093, 64.46
Transmission factors (max,min)	1.00, 0.26	1.00, 0.34
Final R indices [$I>2\sigma(I)$] R_1, wR_2	0.0505, 0.1350	0.0765, 0.2011
R indices (all data) R_1, wR_2	0.0676, 0.1460	0.1007, 0.2148
Largest diff. peak and hole (e Å^{-3})	4.907, −1.434	1.515, −1.959

[a] Weighting scheme, $w=1/(\sigma^2(F_o^2)+(aP)^2+bP)$, where $P=(F_o^2+2F_c^2)/3$.

Table 5
Dimensions in the cooordination sphere of **1** and **2** (Å, °)

Compound **1**	
W(1)–C(300)	1.978(12)
W(1)–C(200)	1.981(12)
W(1)–C(100)	1.988(13)
W(1)–N(21)	2.178(9)
W(1)–N(11)	2.226(9)
W(1)–I(3)	2.8243(11)
W(1)–I(2)	2.8633(9)
C(300)–W(1)–C(200)	103.7(5)
C(300)–W(1)–C(100)	74.9(5)
C(200)–W(1)–C(100)	72.4(5)
C(300)–W(1)–N(21)	82.8(4)
C(200)–W(1)–N(21)	158.6(4)
C(100)–W(1)–N(21)	128.9(4)
C(300)–W(1)–N(11)	160.3(5)
C(200)–W(1)–N(11)	83.6(4)
C(100)–W(1)–N(11)	124.7(4)
N(21)–W(1)–N(11)	84.3(4)
C(300)–W(1)–I(3)	77.7(4)
C(200)–W(1)–I(3)	76.6(3)
C(100)–W(1)–I(3)	131.8(4)
N(21)–W(1)–I(3)	85.1(3)
N(11)–W(1)–I(3)	86.5(2)
C(300)–W(1)–I(2)	113.6(4)
C(200)–W(1)–I(2)	117.1(3)
C(100)–W(1)–I(2)	71.0(4)
N(21)–W(1)–I(2)	77.2(3)
N(11)–W(1)–I(2)	77.6(2)
I(3)–W(1)–I(2)	157.2(3)
Compound **2**	
W(1)–C(100)	1.899(19)
W(1)–C(300)	2.000(16)
W(1)–C(200)	2.02(2)
W(1)–N(11)	2.204(15)
W(1)–As(1)	2.6552(17)
W(1)–I(3)	2.8465(14)
W(1)–I(2)	2.8596(11)
C(100)–W(1)–C(300)	71.8(7)
C(100)–W(1)–C(200)	73.8(7)
C(300)–W(1)–C(200)	107.1(7)
C(100)–W(1)–N(11)	128.2(6)
C(300)–W(1)–N(11)	82.8(5)
C(200)–W(1)–N(11)	158.0(6)
C(100)–W(1)–As(1)	72.0(5)
C(300)–W(1)–As(1)	113.0(4)
C(200)–W(1)–As(1)	113.9(6)
N(1)–W(1)–As(1)	78.2(3)
C(100)–W(1)–I(3)	129.2(5)
C(300)–W(1)–I(3)	77.5(5)
C(200)–W(1)–I(3)	78.0(6)
N(11)–W(1)–I(3)	85.4(4)
As(1)–W(1)–I(3)	158.81(5)
C(100)–W(1)–I(2)	126.3(6)
C(300)–W(1)–I(2)	161.4(5)
C(200)–W(1)–I(2)	77.5(5)
N(11)–W(1)–I(2)	87.2(3)
As(1)–W(1)–I(2)	79.88(4)
I(3)–W(1)–I(2)	86.15(4)

3.3.3. Structure analysis and refinement

In both structures the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An empirical absorption correction was made using the DIFABS program [16]. Both structures were then refined on F^2 using SHELXL [17]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

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