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SOLID STATE STRUCTURES AND ^{13}C NMR SPECTRA OF THE SEVEN-COORDINATE COMPLEXES [$WI_2(CO)_3(NCR)_2$] (R = Me or Et)

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Abstract—The X-ray crystal structures of the two seven-coordinate complexes [$WI_2(CO)_3(NCR)_2$] {R = Me (**1**) or Et (**2**)} have been determined. In both structures, the molecules have crystallographic *m* symmetry. The geometries of the metal coordination spheres are very similar, conforming reasonably well to distorted capped octahedra. The ^{13}C NMR spectra of **1** and **2** are also described, and for the case of complex **1** can be correlated with the crystallographically observed geometry.

In 1960, Nigam *et al.*[1] described the preparation of the seven-coordinate complexes [$MoX_2(CO)_3$(diars)] (X = Br or I; diars = 1,2-$Me_2AsC_6H_4AsMe_2$). Since this early report the synthesis and molecular structures of seven-coordinate complexes of molybdenum(II) and tungsten(II) have been widely explored.[2–11] The structures of seven-coordinate complexes have generally been found[12,13] to have (i) capped octahedral, (ii) capped trigonal prismatic, (iii) pentagonal bipyramidal, or (iv) the so-called "4:3" geometry. The most common geometry for complexes of the type [$MX_2(CO)_3L_2$] (M = Mo or W; X = halide; L = neutral donor ligand) is capped octahedral.[14] In 1982, Colton and Kevekordes[15] described how ^{13}C NMR spectroscopy could be used to correlate the solid state structure with the carbonyl region of the solution state ^{13}C NMR spectrum for a capped octahedral complex containing a carbonyl ligand in the unique capping position.

In this paper we describe the X-ray crystal structures and ^{13}C NMR spectra of the seven-coordinate bis(nitrile) complexes [$WI_2(CO)_3(NCR)_2$] (R = Me or Et). A communication describing part of this work[16] has been reported previously.

EXPERIMENTAL

The complex [$WI_2(CO)_3(NCMe)_2$] (**1**) was prepared by reacting *fac*-[$WI_2(CO)_3(NCMe)_3$] (prepared *in situ*) with an equimolar amount of I_2 at 0°C,[17] whereas the bis(proprionitrile) complex [$WI_2(CO)_3(NCEt)_2$] (**2**) was prepared by reacting [$WI_2(CO)_3(NCMe)_2$] with an excess of NCEt in CH_2Cl_2 at room temperature.[18] The ^{13}C NMR spectra for the seven-coordinate bis(nitrile) complexes [$WI_2(CO)_3(NCR)_2$] (R = Me or Et) were recorded

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on a Bruker WH-400 MHz NMR spectrometer at the University of Warwick. All spectra were referenced to tetramethylsilane.

Crystals suitable for X-ray crystallography were obtained by cooling an acetonitrile solution of **1** and a CH_2Cl_2–Et_2O (80 : 20) solution of **2** at −17°C.

Crystallography

Crystal data for **1** and **2** are given in Table 1. For **1** the crystal was set up to rotate about the *a*-axis on a Stoe STADI2 diffractometer and data were collected via variable width ω scan. Background counts were for 20 s and a scan rate of 0.033°/s was applied to a width of $(1.5+\sin \mu/\tan \theta)$. An empirical absorption correction was applied.[19] The structure was determined by the heavy atom method. All non-hydrogen atoms were refined anisotropically. The methyl hydrogen atoms were refined as a rigid group. The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F)+0.003F^2]$ and the structure refined on *F* using SHELX76.[20]

For **2** the data were collected using the MARresearch Image Plate System. The crystals were positioned at 75 mm from the Image Plate. Ninety frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[21] The structure was solved using heavy atom methods. Methylene hydrogen atoms were included in calculated positions and methyl groups refined as rigid groups. All non-hydrogen atoms were refined using anisotropic thermal parameters. The structure was refined on F^2 using SHELXL.[22] Calculations for **1** were carried out on an Amdahl 5870 computer, and for **2** on a Silicon Graphics workstation, both at the University of Reading. The final dimensions for **1** and **2** are given in Tables 1 and 2. Supplementary Publication Material includes positional parameters, anisotropic thermal parameters, hydrogen positions, remaining dimensions and structure factor tables.

RESULTS AND DISCUSSION

The tungsten bis(acetonitrile) complex $[WI_2(CO)_3(NCMe)_2]$ (**1**) was prepared by reacting

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

	1	**2**
Formula	$C_7H_6N_2O_3I_2W$	$C_9H_{10}I_2N_2O_3W$
Cell weight	2415.2	2527.36
Temperature (K)	293 (2)	293 (2)
Wavelength (Å)	0.7107	0.7107
Crystal system	Orthorhombic	Monoclinic
Space group	*Pmnb* (no. 62)	*C2/m*
Unit cell dimensions: *a* (Å)	12.405 (8)	16.458 (10)
b (Å)	7.590 (8)	13.506 (10)
c (Å)	13.844 (12)	7.331 (10)
β (°)	(90)	105.5 (1)
Volume (Å^3)	1303.5	1570
z	4	4
D_{calc} (Mg m^{-3})	3.02	2.68
Absorption coefficient (mm^{-1})	13.98	11.29
F(000)	1064	1128
Crystal size (mm^3)	0.25 × 0.3 × 0.3	0.2 × 0.2 × 0.2
θ range for data collection (°)	3–25	3.02–25.46
Index ranges	$0 \leq h \leq 14$	$0 \leq h \leq 19$
	$0 \leq k \leq 9$	$0 \leq k \leq 16$
	$0 \leq l \leq 22$	$-8 \leq l \leq 7$
Independent reflections measured	1264	1187
Independent reflections above background	911 [$I > 3\sigma(I)$]	1036 [$I > 4\sigma(I)$]
Data/parameters	911/80	1036/88
Goodness-of-fit	0.873	0.546
R index	0.074 [$I > 3\sigma(I)$]	0.056 [$I > 4\sigma(I)$]
Largest diff. peak and hole (e Å^{-3})	2.74, −3.21	1.77, −2.97

Table 2. Bond lengths (Å) and angles (°) for **1** and **2**

	1	**2**
W(1)—I(1)	2.846 (2)	2.864 (3)
W(1)—I(2)	2.797 (2)	2.828 (2)
W(1)—C(1)	1.99 (3)	2.02 (2)
W(1)—C(2)	2.03 (3)	1.97 (2)
W(1)—N(3)	2.17 (2)	2.18 (1)
C(1)—O(1)	1.12 (4)	1.09 (2)
C(2)—O(2)	1.05 (3)	1.15 (2)
N(3)—C(3)	1.20 (2)	1.13 (2)
C(3)—C(4)	1.42 (3)	1.44 (2)
C(4)—C(5)	—	1.58 (2)
I(1)—W(1)—(2)	160.3 (9)	158.3 (1)
I(1)—W(1)—C(1)	69.0 (7)	72.3 (6)
I(2)—W(1)—C(1)	130.7 (7)	129.4 (6)
I(1)—W(1)—C(2)	114.2 (6)	115.0 (5)
I(2)—W(1)—C(2)	76.5 (7)	77.1 (5)
C(1)—W(1)—C(2)	74.0 (8)	72.0 (6)
I(1)—W(1)—N(3)	81.2 (4)	78.7 (4)
I(2)—W(1)—N(3)	83.9 (4)	85.1 (4)
C(1)—W(1)—N(3)	129.8 (6)	128.9 (5)
C(2)—W(1)—N(3)	156.1 (9)	158.8 (6)
C(2)—W(1)—C(2*)	104.5 (10)	102.7 (9)
C(2)—W(1)—N(3*)	83.6 (9)	84.0 (6)
N(3)—W(1)—N(3*)	80.9 (6)	83.2 (6)
W(1)—C(1)—O(1)	171 (2)	179 (2)
W(1)—C(2)—O(1)	176 (2)	178 (2)
W(1)—N(3)—C(3)	168 (2)	175 (1)
N(3)—C(3)—C(3)	180 (2)	178 (2)
C(3)—C(4)—C(5)	—	114 (1)

Symmetry elements represented by asterisks: in **1**, $0.5-x, y, z$; in **2**, $x, -y, z$.

the zero-valent six-coordinate complex *fac*-[$WI_2(CO)_3(NCMe)_e$] (prepared *in situ*) with an equimolar amount of I_2 at 0°C.[17] However, the bis(proprionitrile) analogue [$WI_2(CO)_3(NCEt)_2$] (**2**) was prepared by reacting [$WI_2(CO)_3(NCMe)_2$] with an excess of NCEt in CH_2Cl_2 at room temperature.[18] Suitable single crystals for X-ray crystallography were grown of complexes **1** and **2** by cooling (− 17°C) solutions of these materials in either acetonitrile (complex **1**) or in a CH_2Cl_2–Et_2O (80 : 20) mixture (complex **2**).

The two structures have very similar geometries as described by the dimensions in Table 2 and illustrated in Figs 1 and 2, together with the common atomic numbering scheme. Both structures have crystallographically imposed mirror symmetry and the metal environment can best be described as distorted capped octahedral with one carbonyl in the unique capping position [W(1)—C(1) 1.99 (3) and 2.02 (2) Å in **1** and **2**, respectively]. The capped face contains one iodine atom [W—I(1) 2.846 (2), 2.864 (3) Å], and two crystallographically equivalent carbonyl groups [W—C(2) 2.03 (3), 1.97 (2) Å]. The remaining iodine atom [W—I(2) 2.797 (2), 2.828 (2) Å] occupies the uncapped face together with two crystallographically equivalent nitrile groups [2.17 (2), 2.18 (1) Å].

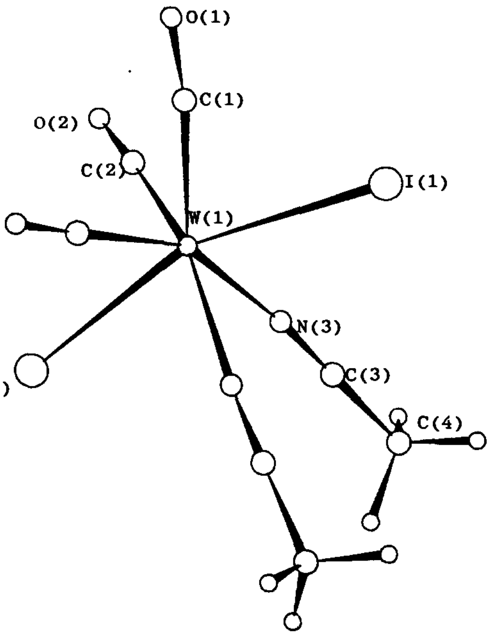

Fig. 1. X-ray crystal structure of [$WI_2(CO)_3(NCMe)_2$] (**1**) showing the atomic numbering scheme.

Using our method[12] for the calculation of r.m.s. deviations from ideal geometries, we find that after normalization of bond lengths, the present geometries have r.m.s. deviations of 0.042 and 0.038

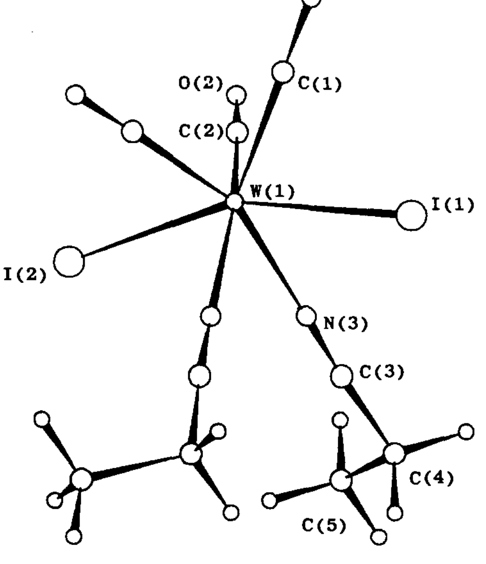

Fig. 2. X-ray crystal structure of [$WI_2(CO)_3(NCEt)_2$] (**2**) showing the atomic numbering scheme.

Å respectively from the ideal capped octahedron. These are surprisingly low figures in view of the distortions in the capped and uncapped faces caused by the large iodine atoms.

The iodine atoms are mutually *trans* and it is noteworthy that the W—I bond to the iodine in the capped face is significantly longer in both structures than the bond to the uncapped face (differences 0.049 and 0.036 Å). This is presumably due to the greater crowding in the capped face. Remaining dimensions are as expected.

The room temperature ^{13}C NMR (+25°C, CD_2Cl_2) spectrum of **1** shows one carbonyl resonance at δ 219.64 ppm, which implies there is a fluxional process occurring whereby the three carbonyl ligands are appearing in the same environment at room temperature. The low temperature (−70°C, CD_2Cl_2) ^{13}C NMR spectrum of **1** shows two carbonyl resonances at δ 228.48 and 202.36 ppm with an intensity ratio of 1 : 2. From Colton and Kevekordes'[15] observations it is very likely that the low field resonance at δ 228.48 ppm is due to the unique capping carbonyl and the resonance at δ 202.36 ppm is due to the two equivalent octahedral carbonyl ligands. However, the low temperature ^{13}C NMR spectrum (−70°C, CD_2Cl_2) for complex **2** shows a single resonance at δ 220.66 ppm, which suggests that the complex is still undergoing a rapid fluxional process even at −70°C.

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