The Crystal Structure and Low Temperature $^{13}$C NMR Spectrum of the Seven-Coordinate Complex of Tungsten(II), [WI$_2$(CO)$_3$(NCPh)$_2$]

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The crystal structure of [WI$_2$(CO)$_3$(NCPh)$_2$] (I) has been determined by X-ray methods. The crystals are orthorhombic, space group Pnam, $a = 7.815(3)$, $b = 13.839(5)$, $c = 18.475(3)$ Å, $Z = 8$, $R = 0.0346$ for 1497 observed data. The complex [WI$_2$(CO)$_3$(NCPh)$_2$] has a seven-coordinate geometry, which may be described as a distorted capped octahedron, with the two iodo-ligands mutually trans, while each nitrile is trans to a carbonyl group. The capped octahedral geometry consists of a capping carbonyl [C(10)] on the face defined by I(1), C(20) and C(20)#. However, the geometry may also be described as a capped trigonal prism, which has one triangular face occupied by three carbonyl groups and the second triangular face occupied by N(1), N(1)# and I(1) atoms, respectively. The iodide I(2) occupies the capping position on the rectangular face defined by the atoms C(20), C(20)#, N(1), and N(1)φ. The low temperature $^{13}$C NMR spectrum (203 K, CD$_2$Cl$_2$) of I shows a single carbonyl resonance at 219.27 ppm which indicates that the complex is undergoing a rapid fluxional process in solution at 203 K.

Introduction

Seven-coordination is much less commonly observed in transition-metal complexes compared to, for example, four and six-coordinate geometries. However, seven-coordinate carbonyl complexes of molybdenum(II) and tungsten(II) are very common [1 – 6], mainly because they obey the effective atomic number rule. The most common geometries for seven-coordinate complexes [7, 8] are (i) capped octahedral, (ii) capped trigonal prismatic, (iii) pentagonal bipyramidal, and (iv) the “4:3 geometry”, or piano-stool geometry. A survey [9] has shown that the most common geometry for complexes of the type [MX$_3$(CO)$_2$L]$_2$ (M = Mo or W; X = halide; L = neutral monodentate donor ligand) is capped octahedral. Colton and Kevekordes [10] have shown how the solid state capped octahedral structures of seven-coordinate complexes of molybdenum(II) and tungsten(II) can be correlated with the solution state structures by the use of $^{13}$C NMR spectroscopy in the carbonyl region of the spectrum.

In this paper we describe the X-ray crystal structure and low temperature $^{13}$C NMR spectrum (carbonyl region) of the bis(benzonitrile) complex [WI$_2$(CO)$_3$(NCPh)$_2$] (I).

Results and Discussion

The complex [WI$_2$(CO)$_3$(NCPh)$_2$] (I) was prepared [11] by reacting the bis(acetonitrile) complex [WI$_2$(CO)$_3$(NCMe)$_2$] with an excess of NCPh in CH$_2$Cl$_2$ at room temperature. Single crystals of [WI$_2$(CO)$_3$(NCPh)$_2$] (I) suitable for X-ray crystallography were grown from a CH$_2$Cl$_2$/Et$_2$O mixture (80:20) at ~17 °C. The molecular structure of [WI$_2$(CO)$_3$(NCPh)$_2$] (I) is shown in Fig. I, together with the atomic numbering scheme. Atomic coordinates and bond lengths and angles are given in Tables I and II, respectively.

Crystals of I are composed of discrete molecules of [WI$_2$(CO)$_3$(NCPh)$_2$] (I), which are held together by Van der Waals forces. Complex I has seven-coordinate geometry, which could be described as a distorted capped octahedron, with...
analogous ligand dispositions (see Fig. 2a). The two iodide ligands are trans to each other, whilst each nitrile ligand is trans to a carbonyl group. The capped octahedral geometry has a capping carbonyl C(10) on the face defined by I(1), C(20), C(20)#. However, the geometry can also be considered as a capped trigonal prism, with one triangular face occupied by the three carbonyl ligands and a second triangular face consisting of the N(1), N(1)#, I(1) atoms. The remaining iodide I(2) occupies the capping position on the rect-

Table I. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for [WI_2(CO)_3(NCPh)_2]. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

<table>
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<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U_{eq}</th>
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<td>2500</td>
<td>20(1)</td>
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<tr>
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<td>8237(1)</td>
<td>2500</td>
<td>21(1)</td>
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<td>9862(1)</td>
<td>2500</td>
<td>11(1)</td>
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<td>10459(4)</td>
<td>3292(3)</td>
<td>18(1)</td>
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<tr>
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The molecular structures of the analogous bis(nitrile) complexes [WI_2(CO)_3(NCR)_2] (R = Me or Et) [12] have been previously determined. The structure of these complexes have distorted octahedral geometries with carbonyl groups in the unique capping position. All three complexes [WI_2(CO)_3(NCR)_2] (R = Me [12], Et [12], or Ph [this paper]) have very similar dispositions of seven ligands around the tungsten centre. The two iodides are trans to each other, and the acetonitrile ligand is trans to a carbonyl group. A comparison of analogous bond lengths shows only small differences. However, the W–C(CO) distances of the two equidistant carbonyl groups are slightly longer for [WI_2(CO)_3(NCMe)_2] than the analogous distances in both (I) [197.7(7) pm] and [WI_2(CO)_3(NCMe)_2] [197.0(2) pm]. The capping carbonyl for [WI_2(CO)_3(NCMe)_2] has the shortest W–C(CO) bond length [199.1(2) pm]. The bond angles in [WI_2(CO)_3(NCMe)_2] also show small deviations from their respective values in I and [WI_2(CO)_3(NCMe)_2]. The N–C–C bond angle of [180(2)°] in [WI_2(CO)_3(NCMe)_2] is linear, although the analogous angles in I and
[WI₂(CO)₃(NCMe)₂] deviate by 2° from linearity. The W-C-O angles in 1 and [WI₂(CO)₃(NCMe)₂] are almost linear, whereas the respective angles in [WI₂(CO)₃(NCPh)₂] [171(2)°, 176(2)°] have a greater deviation from linearity.

Colton and Kevekordes [10] have used ¹³C NMR spectroscopy to correlate the frequency of a carbonyl ligand and its position around the metal centre. For example, in accord with Colton and Kevekordes’ [10] proposal, the low temperature (203 K, CD₂C₁₂) ¹³C NMR spectrum of [WI₂(CO)₃(NCMe)₂] has two resonances at 228.48 and 202.36 ppm in a ratio of 1:2, which is consistent with the capped octahedral structure shown in Fig. 1 for [WI₂(CO)₃(NCPh)₂]. The resonance at the higher frequency δ = 228.48 ppm was attributed to the capping carbonyl, which has the shortest W-C(CO) bond length [199.1(26) pm], whilst the resonance at δ = 202.36 ppm corresponds to the two equivalent octahedral carbonyl ligands.

The low temperature (203 K, CD₂Cl₂) ¹³C NMR spectrum for the crystallographically characterized complex [WI₂(CO)₃(NCPh)₂] (1) showed a single carbonyl resonance at δ = 219.27 ppm which indicates that the complex is undergoing a rapid fluxional process at 203 K, i.e. faster than the NMR time scale. Due to problems of solubility and solvents at low temperature it was not possible to go to lower temperature, however it might be expected that a similar pattern as was found for [WI₂(CO)₃(NCMe)₂] [12] would be observed at a lower temperature.

**Experimental**

The complex [WI₂(CO)₃(NCPh)₂] was prepared by the literature method [11]. The ¹³C NMR spectrum (203 K, CD₂Cl₂) was recorded on a Bruker WH 400 MHz NMR spectrometer at the University of Warwick, referenced to tetramethylsilane. Single crystals suitable for X-ray crystallography were obtained from a cooled (256 K) CH₂C₁₂/Et₂O (80:20) solution of [WI₂(CO)₃(NCPh)₂] (1).

**Crystallography**

A crystal of dimensions 0.24×0.18×0.18 mm was mounted on a glass fibre under silicone oil.

**Crystal data.** C₁₇H₁₀I₂N₂O₃W. Mᵣ = 363.96, Orthorhombic, a = 7.815(3), b = 13.839(5), c = 18.475(3) Å, U = 1998.1(11) Å³, Space group Pnam (alternative No. 62), Z = 8, Dₑ = 2.42 g cm⁻³, F(000) = 1320, μ = 8.888 mm⁻¹.

**Data collection and processing.** Data were collected on a Delft Instruments FAST TV area detector diffractometer at the window of a rotating anode FR591 generator (50 kV, 40 mA), with a molybdenum target (λMo-Kα = 0.71069 Å), controlled by a Micro Vax 3200 and driven by MADNES [13] software. Data were collected at 150 K using an Oxford Cryostream low temperature cooling system. 5755 reflections collected (1.84 < θ < 24.94°), index ranges −9 < h < 6;
-15 < k < 15; -19 < l < 20, giving 1643 unique data \( R_{\text{int}} = 0.085 \) after absorption correction, (DIFFABS) [14].

Structure analysis and refinement. The structure was solved by heavy atom methods (SHELX-S [15]) and then subjected to full-matrix least squares refinement based on \( F_0^2 \) (SHELX-93 [16]). Non hydrogen atoms were refined anisotropically with all hydrogens included in idealized positions (C–H distance = 0.97 Å, C/H–C–C angles = 109.5°) with isotropic thermal parameters free to refine. The weighting scheme used was \( w = 1/\sigma^2(F_0^2) \).

Final \( wR^2 \) and \( R \) values are 0.0813 and 0.0378 respectively, for all 1643 data and 126 parameters (\( \sigma_{\text{max}} = \sigma_{\text{min}} \)). The corresponding \( wR^2 \) and \( R \) values for 1479 data with \( F_0 > 4\sigma(F_0) \) are 0.0780 and 0.0346 respectively. Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

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