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THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRACARBONYL(6-*p*-STYRYL-2,2′-BIPYRIDYL)TUNGSTEN(0). AN EXAMINATION OF THE AFFECT OF A BULKY GROUP α TO ONE COORDINATING NITROGEN ATOM IN A BIDENTATE LIGAND

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Summary

The crystal and molecular structure of tetracarbonyl(6-*p*-styryl-2,2′-bipyridyl)-tungsten(0) have been determined by single crystal X-ray techniques. Cell dimensions are *a* 13.735(17), *b* 8.839(6) and *c* 17.105(12) Å for the monoclinic unit cell with β 109.06(8)° and $Z = 4$. The space group was determined as $P2_1/n$. The structure was solved by conventional Patterson and Fourier methods and refined to a final *R*-value of 0.055 (1734 unique reflections) by block diagonal least squares. The molecule consists of monomeric units containing one tungsten atom bound to four terminal carbonyl groups and to one 6-*p*-styryl-2,2′-bipyridyl ligand via its two nitrogen atoms. The presence of the styryl group α to one coordinating nitrogen causes a significant difference in the bond lengths between the central tungsten atom and the nitrogen atoms (W–N(1), 2.29(1) Å; W–N(2) 2.23(1) Å).

Introduction

Our continuing interest in the chemistry of polymer-bound metal complexes, has prompted an investigation of the coordinating ability of some vinyl-substituted nitrogen heterocycles [1–4]. It has been shown that the initial formation of complexes containing polymerisable groups, followed by copolymerisation with suitable comonomers should yield polymers with well defined metal centres [2,4]. Another approach, of functionalising ready-made polymers and treating these with metal

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complexes, may present problems in determining the exact nature of coordination [5]. For this reason, we have synthesised a number of vinyl-pyridine complexes of ruthenium [4], and the Group VI pentacarbonyls [2].

Recently, metal complexes of polystyrene-2,2′-bipyridine have been synthesised [5–12] and shown to have applications as hydrogenation catalysts [8]. It was assumed that the attachment of the 2,2′-bipyridyl group to the polystyrene is via the C(6) carbon on the bipyridyl ring [13]. This might result in the labilizing of the bipyridyl–metal bonds because of steric interactions, a feature which could improve the catalytic ability of the polymer bound complexes. In order to obtain a better understanding of such systems a number of metal complexes of 6-*p*-styryl-2,2′-bipyridyl were synthesised and their spectroscopic properties were examined [14]. In particular proton NMR spectra provided some interesting information about the structure of the compounds.

A study of the ^{1}H NMR spectrum of $[Ru(bipy)_2(6\text{-}p\text{-styryl-2,2'-bipyridyl})]^{2+}$, (bipy = 2,2′-bipyridyl), in the temperature range 0–70 °C, revealed that the broadening of the arene proton resonances, observed at room temperature, is due to a hindered rotation of the styryl group relative to the bipyridyl ring. In the ^{1}H NMR spectrum of $W(CO)_4$ (6-*p*-styryl-2,2′-bipyridyl) (I) however, no broadening was observed at room temperature.

In this paper we present the crystal and molecular structure of I, allowing the influence of the bulky styryl group α to one coordinating nitrogen on both the structure and spectroscopic properties of the complex to be examined.

Experimental

The synthesis of I has been described elsewhere [14]. Crystals of this dark red material were grown from a toluene/chloroform mixture (50/50 v/v). Although the complex appears to be stable to air both in the solid state and in solution, precautions were taken to minimise exposure to light while in solution.

Determination of the crystal structure of I

A chunky hexagonal crystal of I about 0.1 mm in diameter and about 0.05 mm thick was selected for unit cell determination and intensity data collection on a Nicolet P3 four circle diffractometer with graphite monochromated radiation (λ 0.7107 Å). The unit cell is monoclinic ($Z = 4$) with a 13.735(17), b 8.839(6) and c 17.105(12) Å and β 109.06(8)° and gives a calculated density of 1.875 g/cm^3 for a molecular weight of 554.22. The space group is uniquely defined from the systematic absences as $P2_1/n$ (a non-standard setting of $P2_1/c$, No. 14). The intensities of 1734 unique reflections ($2\theta \leqslant 40$) were measured using the $\theta/2\theta$ scan technique. The intensities of two reference reflections measured at intervals of 50 reflections throughout data collection showed no significant variation. No absorption correction was applied and the intensities were converted to structure amplitudes in the usual way. The structure determination was completed on the basis of 1659 observed reflections ($I > 2\sigma$). All calculations were carried out on the Honeywell 66/80 machine of the Computing Centre of the University of Aberdeen using the NRC programs of F.R. Ahmed and his collaborators [15]. Atomic scattering factors for neutral atoms were taken from International Tables [16].

The structure was solved by conventional Patterson and Fourier methods and refined to final R-value of 0.055 by block diagonal least squares. In the last stages of refinement the weight scheme $W = 1/[1 + \{(F_o - P(2))/P(1)\}^2]$ with $P(1) = 40$ and $P(2) = 70$ was used and the tungsten atom was allowed to vibrate anisotropically. At this stage the distributions of $\Sigma w \Delta F$ aganst $\sin^2\theta$ and $[F_o]$ were satisfactory and the difference map was essentially featureless. No attempt was made to establish the positions of the hydrogen atoms. The final positional and thermal vibration parameters are given in Table 1 and selected bond lengths and angles in Table 2. Lists of F_o/F_c are available from the authors. Figure 1 shows the shape of the molecule and the atom numbering scheme.

Description of the structure of I

Each molecule consists of one tungsten atom bound to four carbonyl groups, and to one 6-*p*-styryl-2,2′-bipyridyl ligand via its two nitrogen atoms. The shape of the

TABLE 1

POSITIONAL AND THERMAL VIBRATION PARAMETERS FOR I (Fractional coordinates are $\times 10^5$ for W and $\times 10^4$ for all other atoms. E.s.d.'s applicable to the least significant digit are given in parentheses.)

Atom	x/a	y/b	z/c	B_{iso}(Å^2)
W	41539(5)	17189(7)	63910(4)	3.43 [a]
N(1)	3538(9)	4114(14)	6007(7)	3.6(2)
N(2)	5489(9)	3175(14)	6421(7)	3.7(2)
O(1)	2224(9)	−305(14)	6228(7)	5.4(3)
O(2)	4364(12)	1911(17)	8288(9)	7.8(3)
O(3)	5438(9)	−1222(14)	6921(8)	5.6(3)
O(4)	3706(9)	519(14)	4573(8)	6.1(3)
C(1)	2911(11)	481(17)	6290(9)	3.7(3)
C(2)	4334(13)	1965(20)	7587(10)	4.7(4)
C(3)	4938(12)	−128(20)	6717(10)	4.4(3)
C(4)	3898(11)	1047(18)	5236(9)	3.6(3)
C(11)	4232(11)	5134(19)	5917(9)	3.9(3)
C(12)	3924(14)	6577(22)	5548(11)	5.4(4)
C(13)	2912(15)	6934(23)	5308(12)	6.1(4)
C(14)	2220(14)	5915(22)	5432(11)	5.4(4)
C(15)	2549(12)	4492(18)	5809(10)	4.2(3)
C(21)	5325(12)	4657(19)	6187(10)	4.2(3)
C(22)	6116(14)	5666(20)	6225(11)	5.2(4)
C(23)	7107(15)	5120(25)	6508(12)	6.3(4)
C(24)	7327(15)	3606(23)	6735(12)	6.1(4)
C(25)	6450(14)	2666(21)	6686(11)	4.9(4)
C(31)	1800(13)	3561(20)	5983(10)	4.6(4)
C(32)	1857(12)	3280(20)	6824(10)	4.6(3)
C(33)	1111(16)	2439(26)	6991(13)	6.6(5)
C(34)	316(14)	1767(23)	6415(12)	5.9(4)
C(35)	205(16)	2010(23)	5534(12)	6.3(5)
C(36)	947(14)	2912(21)	5335(12)	5.6(4)
C(40)	−461(20)	855(31)	6681(16)	8.9(6)
C(41)	−1152(21)	116(38)	6243(17)	10.4(7)

[a] B_{iso} calculated as $4/3\ (a^2B_{11} + b^2B_{22} + c^2B_{33} + ac\cos\beta B_{13})$.

TABLE 2

BOND LENGTHS (Å) AND ANGLES (°) FOR I E.s.d.'s APPLICABLE TO THE LEAST SIGNIFICANT DIGITS ARE GIVEN IN PARENTHESES

(a) Coordination of W					
W–N(1)	2.29(1)	N(1)–W–N(2)	72.4(4)	C(1)–W–C(2)	88.0(7)
W–N(2)	2.23(1)	N(1)–W–C(1)	104.9(5)	C(1)–W–C(3)	86.7(7)
W–C(1)	1.99(2)	N(1)–W–C(2)	96.0(6)	C(1)–W–C(4)	83.1(6)
W–C(2)	1.99(2)	N(1)–W–C(3)	168.3(6)	C(2)–W–C(3)	85.7(7)
W–C(3)	1.94(2)	N(1)–W–C(4)	93.6(6)	C(2)–W–C(4)	168.4(7)
W–C(4)	1.98(2)	N(2)–W–C(1)	176.1(6)	C(3)–W–C(4)	86.3(7)
		N(2)–W–C(2)	95.1(6)		
		N(2)–W–C(3)	96 0(6)		
		N(2)–W–C(4)	94.2(6)		
(b) Carbonyl groups					
C(1)–O(1)	1.15(2)	W–C(1)–O(1)	176(1)		
C(2)–O(2)	1.19(2)	W–C(2)–O(2)	170(2)		
C(3)–O(3)	1.17(2)	W–C(3)–O(3)	178(1)		
C(4)–O(4)	1.17(2)	W–C(4)–O(4)	173(1)		
(c) Bipyridyl group					
N(1)–C(11)	1.36(2)	N(1)–C(11)–C(12)	122(1)		
C(11)–C(12)	1.42(3)	C(11)–C(12)–C(13)	118(2)		
C(12)–C(13)	1.35(3)	C(12)–C(13)–C(14)	120(2)		
C(13)–C(14)	1.38(3)	C(13)–C(14)–C(15)	121(2)		
C(14)–C(15)	1.42(2)	C(14)–C(15)–N(1)	119(2)		
N(1)–C(15)	1.33(2)	C(15)–N(1)–C(11)	120(1)		
C(11)–C(21)	1.48(2)	C(21)–C(11)–N(1)	117(1)		
N(2)–C(21)	1.37(2)	C(21)–C(11)–C(12)	121(1)		
C(21)–C(22)	1.39(3)	W–N(1)–C(15)	124(1)		
C(22)–C(23)	1.38(3)	W–N(1)–C(11)	116(1)		
C(23)–C(24)	1.40(3)	C(31)–C(15)–N(1)	123(2)		
C(24)–C(25)	1.44(3)	C(31)–C(15)–C(14)	117(2)		
N(2)–C(25)	1.33(2)	N(2)–C(21)–C(22)	122(2)		
		C(21)–C(22)–C(23)	117(2)		
		C(22)–C(23)–C(24)	122(2)		
		C(23)–C(24)–C(25)	116(2)		
		C(24)–C(25)–N(2)	123(2)		
		C(25)–N(2)–C(21)	118(1)		
		C(11)–C(21)–N(2)	114(2)		
		C(11)–C(21)–C(22)	123(2)		
		W–N(2)–C(25)	122(1)		
		W–N(2)–C(21)	119(1)		
(d) Styryl group					
C(31)–C(32)	1.44(2)	C(31)–C(32)–C(33)	120(2)		
C(32)–C(33)	1.37(3)	C(32)–C(33)–C(34)	125(2)		
C(33)–C(34)	1.35(3)	C(33)–C(34)–C(35)	118(2)		
C(34)–C(35)	1.48(3)	C(34)–C(35)–C(36)	119(2)		
C(35)–C(36)	1.42(3)	C(35)–C(36)–C(31)	120(2)		
C(36)–C(31)	1.44(3)	C(36)–C(31)–C(32)	118(2)		
C(40)–C(34)	1.52(3)	C(40)–C(34)–C(33)	120(2)		
C(41)–C(40)	1.20(4)	C(40)–C(34)–C(35)	122(2)		
C(31)–C(15)	1.42(2)	C(15)–C(31)–C(32)	120(2)		
		C(15)–C(31)–C(36)	122(2)		
		C(41)–C(40)–C(34)	126(3)		

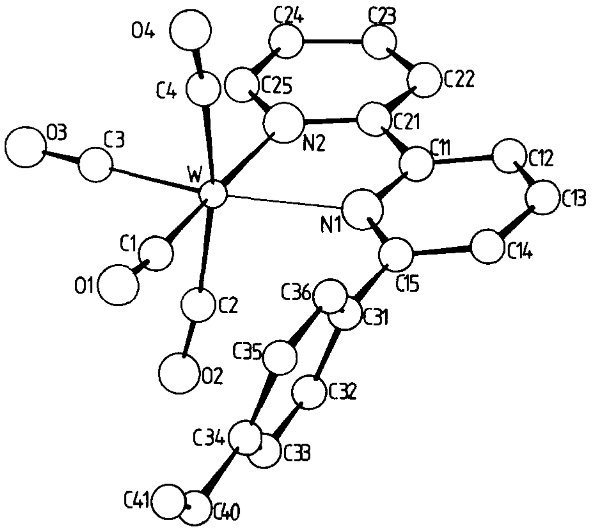

Fig. 1. The molecular structure of I, indicating the numbering system used.

molecule is a distorted octahedron. The two tungsten to nitrogen distances are significantly different, the W–N(1) distance being 2.29(1) Å compared to the W–N(2) distance of 2.23(1) Å. The average tungsten to carbonyl-carbon distance is 1.974 Å, but there is a small variation because of the *trans*-influence of the styryl-bipyridyl ligand. The variation in the metal to carbon distances results in a variation in the carbon to oxygen distances in the predicted manner. The C(1)–O(1) distance being the shortest at 1.15(2) Å and the average being 1.17 Å.

The N(1)–W–C(1) angle is approximately 8° larger than the N(2)–W–C(3) angle, but all other metal centred angles are similar to other tungsten tetracarbonyl complexes [17].

The styryl-bipyridyl ligand appears to be relatively unaffected by coordination to the metal, with all bond lengths and angles similar to these expected for heterocyclic aromatic systems [18]. The two pyridine ring systems are practically co-planar, while the angle between the bipyridyl and styryl ring systems is 111.2°.

Discussion of the structure

It is obvious that the presence of the styryl group hinders the bidentate coordination of the ligand. This results in a considerable lengthening of one tungsten-nitrogen bond and an increase in the N(1)–W–C(1) angle. The W–N(1) bond in this complex (2.29 Å) is longer than those reported for similar complexes such as (di-2-pyridylamine)tetracarbonyltungsten [17] and (3,3,4,4-tetramethyl-3,4-dihydrodiazete)bis(tetracarbonyltungsten) [19] (2.26 and 2.16 Å, respectively). It is argued that both the diazete and pyridylamine ligands are rather poor π-acceptors, and might therefore be expected to have longer tungsten to nitrogen bond lengths than in complexes with ligands of known π-acceptor ability such as 2,2′-bipyridyl. The tungsten to nitrogen bond length in (4-phenyl-1,2,4-triazole)pentacarbonyltungsten has been determined as 2.245(8) Å [20], and the metal to ligand bond in this complex has been shown to be principally σ in character. The length of the W–N(1) bond in I infers a reduction in the thermal stability of this bond when compared with the above complexes, and might be reflected in an increased propensity to form coordinatively unsaturated species.

The orientation of the styryl ring with respect to the bipyridyl ring minimises both the steric interaction with the *cis*-carbonyl and also the interaction between the π-systems of both rings. Recently, the electronic spectra of a number of 4,4′-di-substituted-bipyridyl complexes of $M(CO)_4$ (M = Cr, Mo or W) have been examined [21]. The lowest energy absorption band in these complexes is thought to consist principally of a metal to ligand charge transfer transition, the energy of which is affected by the electronic nature of any substituent on the bipyridyl ligand. The electronic spectrum of I is closely similar to (2,2′-bipyridyl)tetracarbonyltungsten [14,22] and this would imply little or no interaction of the π-systems of the styryl and bipyridyl rings in solution.

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