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Preparation, spectroscopic properties, crystal and molecular structure of pentacarbonyl(3-methyl-1-(pyridin-2-yl)-1,2,4-triazole-N^4)tungsten(0)

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Abstract

The synthesis and molecular structure of pentacarbonyl(3-methyl-1-(pyridin-2-yl)-1,2,4-triazole-N^4)tungsten(0) are described. Surprisingly the ligand is bound to the $W(CO)_5$ moiety via the triazole N^4 (N24) atom, and the pyridine to triazole link is between the pyridine C^2 (C1) atom and the N^1 (N21) atom of the triazole ring. The compound crystallises in the space group $C2/c$ with $a = 24.559(18)$, $b = 9.693(16)$, $c = 13.817(12)$ Å, $\beta = 108.48(12)°$ and $Z = 8$. A full matrix least-squares refinement resulted in a final $R = 0.052$ ($R_w = 0.065$) for 3688 unique reflections.

Introduction

For the past number of years we have been involved in a study of the coordinating properties of potentially chelating ligands. We have shown that ligands such as 2,2′-bipyridine can act as a bridge between two separate metal centres. The subsequent reactions of these materials to produce compounds in which 2,2′-bipyridine coordinates to the metal centre as a chelating ligand have been investigated [1]. Another series of experiments investigated the coordinating properties of asymmetric chelating ligands. Asymmetric chelating ligands are ligands with two chemically distinct coordination sites, such as pyridyltriazoles, pyridyltriazines etc. The photophysical and electrochemical properties of bis(2,2′-bipyridine)-ruthenium compounds with such ligands were studied and the effect of varying the nature of the asymmetric ligand has been investigated [2]. One of the aims of these investigations was to isolate compounds containing potentially chelating ligands which are coordinated in a monodentate fashion. In this contribution we wish to report the synthesis, spectroscopic and structural properties of a tungstenpentacarbonyl compound containing the monodentately coordinated 3-methyl-1-(pyridin-2-yl)-1,2,4-triazole (3Mepytr) ligand. The X-ray structural determination of this compound has been carried out to establish the coordinating mode of this ligand and also to fully characterise the ligand structure, which could not be unambiguously determined using the spectroscopic techniques available.

Experimental

Synthesis of 3-methyl-1-(pyridin-2-yl)-1,2,4-triazole

The ligand was prepared using the Uhlmann condensation as described for the general synthesis of *N*-arylazoles [3]. A mixture of 3(5)-methyl-1,2,4-triazole (2.1 g, 25 mmol), 2-bromopyridine (3.8 g, 24 mmol), anhydrous potassium carbonate (3.6 g) and copper(II) oxide (0.13 g) was heated at reflux temperature in 5 cm^3 of pyridine for 24 h. The cooled mixture was filtered and the residue extracted with chloroform. The chloroform was removed under reduced pressure and the crude product was purified by column chromatography on neutral alumina using chloroform as eluent. The crystals, obtained after evaporation of the solvent, were washed with water, recrystallised from acetone/water mixtures (50/50) and dried *in vacuo* yielding 1.1 g (35%) of the desired product. Melting point 86–87 °C. UV–Vis (methanol): λ_{max} 244, 275 nm. ^{1}H NMR ($CDCl_3$): 2.21 (3H, s, CH_3), 8.89 (1H, s, triazole H^5), 8.29 (1H, d, H^6), 7.83 (1H, t, H^4), 7.67 (1H, d, H^3), 7.21 (1H, t, H^5). Infrared (KBr): 3111(m), 3050(w), 1605(sh), 1592(s), 1575(m), 1529(s), 1476(s), 1458(s), 1310(s), 1248(s),

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1228(s), 1150(m), 1084(m), 1049(m), 997(s), 975(sh), 891(m), 782(s), 735(m), 695(m), 637(w), 620(w), 524(m), 494(m), 428(m), 366(m), 317(m).

Synthesis of $W(CO)_5(3Mepytr)$

$W(CO)_6$ (0.50 g, 1.42 mmol) was exposed to visible irradiation from a medium pressure Hg lamp (400 W) in tetrahydrofuran (THF) (200 cm^3) for 1 h. Following the photolysis this solution was added to a solution containing 0.19 g (1.42 mmol) of 3Mepytr in THF. The solid product was isolated by removal of the solvent and further purified by recrystallisation in toluene/petrol ether solution (50/50). The yellow crystals were then dried *in vacuo*, yielding 0.55 g (87%) of pure material. Melting point 134–135 °C. UV–Vis (methanol): λ_{max} 245, 275(s), 415 nm. ^1H NMR, $CDCl_3$: 2.62 (3H, s, CH_3), 9.38 (1H, s, triazole H^5), 8.49 (1H, d, H^6), 7.90 (2H, m, H^3, H^4), 7.39 (1H, t, H^5). Infrared (KBr ν(CO) stretching region): 2069 (A_1), 2001 (B_1), 1906 (E), 1873 (A_1) cm^{-1}.

Physical measurements

Electronic spectra were recorded on a Hewlett-Packard 8452A UV–VIS spectrometer using 1 cm quartz cuvettes and infrared spectra were obtained as KBr disks using a Perkin-Elmer 983G spectrophotometer. NMR spectra were recorded on the Jeol GX-FT 270 MHz NMR spectrometer of University College, Galway.

X-ray crystallography

A yellow needle shaped crystal of dimensions 0.6×0.4×0.3 mm was selected for X-ray analysis and mounted on a Nicolet P3 four circle diffractometer. Crystal data and data collection parameters are given in Table 1. The unit cell parameters were refined by least-squares procedures and 4272 reflections were recorded at room temperature (with 2θ in the range 0–60°). The intensities of two reference reflections were measured at intervals of 50 reflections throughout the data collection and showed no significant variation. The intensities were converted to structure amplitudes in the usual way and an empirical absorption correction was applied.

Structure solution and refinement

The structure was solved by conventional Patterson and Fourier methods and refined to a final R value of 0.052 ($R_w=0.065$) by full matrix least-squares using SHELX-76 and SHELXS-86 programmes [4]. First isotropic and then anisotropic thermal parameters were used for all non-hydrogen atoms. The hydrogen atoms are at their calculated positions. The function minimised during the least-squares was $\Sigma w(|F_o|-|F_c|)^2$, $w=1.5156(\sigma_F^{-2}+0.01F^2)$. The discrepancy indices are defined as $R=\Sigma|\Delta F|/\Sigma|F_o|$ and $R_w=[\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$. Scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [5].

TABLE 1. Crystal and diffraction data for $W(CO)_5$-(3Mepytr)

Molecular formula	$C_{13}H_8N_4O_5W$
Space group	*C2/c*
a (Å)	24.559(18)
b (Å)	9.693(16)
c (Å)	13.817(12)
β (°)	108.48(12)
V ($Å^3$)	3119(1)
Z	8
$F(000)$	1824
D_{calc} (g cm^{-3})	2.061
Molecular weight	485.09
Crystal dimensions (cm)	0.06×0.04×0.03
Linear absorption (cm^{-1})	75.9
Scan type	$\theta/2\theta$
Scan speed (° 2θ/min)	5.33–58.6
Scan width (° 2θ)	2.4–2.8
Radiation (Å)	$\lambda=0.7107$
2θ range (°)	3.5–60
Transmission factors, min.; max.	0.0264; 0.1336
Reflections measured	$0(0,\ -20)\leq h(k,\ l)\leq 36(15,\ 20)$
Unique total data	4272
Unique observed data ($I>3\sigma$)	3688

Results and discussion

Synthesis

The ligand synthesis is based on the coupling of 2-bromopyridine and 3(5)methyl-1,2,4-triazole via the elimination of HBr [3]. This results in a pyridyltriazole compound in which the two rings are bound via the alpha-carbon on the pyridine ring and either the N^1 or the N^2 nitrogen on the triazole ring. In earlier work [2], using unsubstituted 1,2,4-triazole, only one product was obtained from this reaction because the N^1 and N^2 nitrogens are equivalent and bonding through N^4 is not observed. However, in the present synthesis the N^1 and N^2 positions of the triazole ring are no longer equivalent because of the presence of the methyl substituent on the triazole ring. Therefore, because of the poorly defined position of the triazole hydrogen in the starting material two products are possible from this reaction, one in which the pyridine–triazole link is alpha to the methyl substituent on the triazole ring, and the other in which the link is beta to the methyl group. Not withstanding this potential difficulty, the preparation of the pyridyltriazole compound from 3(5)methyl-1,2,4-triazole by this route proved satisfactory with the isolation of a single product in a reasonable yield. The W(CO)$_5$(3Mepytr) complex was prepared by a well established route [1]. No evidence was obtained, by IR spectroscopy, for the formation of tetracarbonyl containing products, which would result from the bidentate coordination of the pyridyltriazole ligand. The compound was isolated as a yellow air-stable solid in high yield.

Spectroscopic properties

Both the ligand and the metal compound were examined using ^{1}H NMR, IR and UV–Vis spectroscopy. The data obtained for the ligand did not yield any definite evidence about the position of the pyridine–triazole bond. An assignment of the proton NMR has been given in 'Experimental' and is based on comparison with spectra of analogous compounds [2].

The IR spectrum of the complex clearly indicates the presence of a metal pentacarbonyl moiety, the bands being readily assigned to the two A$_1$ and the E mode of the pseudo C_{4v} metal centre, by comparison with other monosubstituted metal hexacarbonyl derivatives [6]. Three possible binding sites exist on the ligand, two based on the triazole ring and one on the pyridine ring. It was not possible to unambiguously determine the mode of coordination of the ligand to the metal pentacarbonyl moiety using only spectroscopic techniques. ^{1}H NMR spectroscopy in general is an excellent technique for examining species of the type M(CO)$_5$(L) (L = heterocyclic ligand) as only the ligand contributes to the spectrum. Therefore, it is relatively easy to compare the ^{1}H NMR spectrum of the ligand to that of the metal complex. The ^{1}H NMR spectrum of W(CO)$_5$(3Mepytr) exhibits some substantial shifts when compared to the uncoordinated ligand. The most significant shifts are observed for the methyl group protons (+0.4 ppm with respect to the free ligand) and the triazole proton (+0.5 ppm). However, small downfield shifts are also observed for the pyridine H^6 and H^4 protons. It is interesting to compare the NMR data obtained for this compound with those reported earlier for a series of related triazole containing metalpentacarbonyl compounds. The ligands investigated were 4-phenyl-1,2,4-triazole (4Phtrz) and 4-methyl-1,2,4-triazole (4Metrz). Contrary to the results obtained for the 3Mepytr complex, in compounds containing 4Metrz the methyl resonance was shifted to slightly higher field (−0.1 ppm) upon coordination [7]. This would indicate that for the 3Mepytr compound, both the triazole proton and the methyl group are close to the nitrogen atom involved in coordination to the tungsten atom (i.e. N^4), while in the 4Metrz compound the methyl group is pointing away from the metal carbonyl moiety [2]. Of the two triazole protons observed in M(CO)$_5$(L) (L = 4Metrz or 4Phtrz; M = Cr, Mo or W) one shifts to higher field while the other is shifted downfield. The results reported here suggest that the resonance observed at lower field in the 4Phtrz and 4Metrz complexes can be assigned to the protons adjacent to the coordinating nitrogen atom.

Description of the structure of W(CO)$_5$(3Mepyrtr)

The molecular structure of W(CO)$_5$(3Mepyrtr) is given in Fig. 1. The fractional coordinates and the bond lengths and angles for this molecule are given in Tables 2 and 3. See also 'Supplementary material'. The structural determination shows the triazole ring to be bound to the pyridine ring via the N21 (N^1) atom. Five carbonyl ligands coordinate to the tungsten atom as indicated by the IR spectrum and the pyridyltriazole ligand is, surprisingly, coordinated to the tungsten atom via the N24 (N^4) atom of the triazole ring. This confirms the conclusions drawn from the ^{1}H NMR spectrum of this compound. The tungsten atom is, therefore, in a slightly distorted octahedral coordination sphere. The tungsten to nitrogen distance is 2.273(7) Å, a value that is in the range expected for this type of bond [6]. The tungsten to carbon bond lengths vary in a manner appropriate for this class of compound, the metal to carbon vector *trans* to the triazole ligand being significantly shorter at 1.974(10) Å than the other four tungsten to carbon vectors. This can be explained by the reduced π-acceptor properties of the pyri-

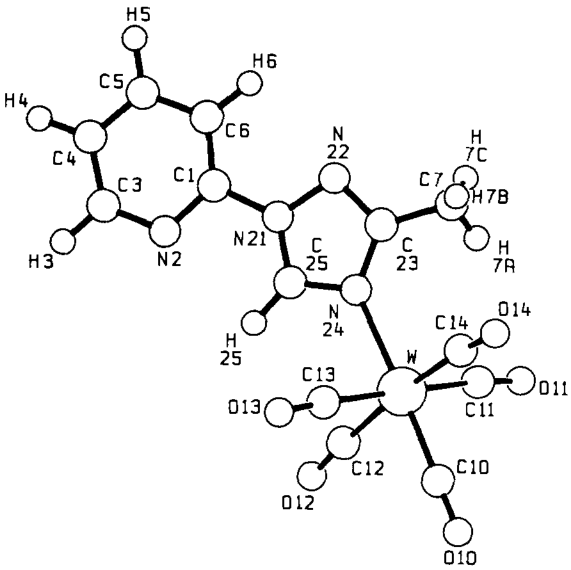

Fig. 1. Molecular structure of W(CO)$_5$(3Mepyrtr).

TABLE 2. $W(CO)_5$(Metrpy) coordinates ($\times 10^4$) with e.s.d.s in parentheses

	x/a	y/b	z/c	$U_{eq}{}^a \times 10^3$
W	6385(1)	482(1)	2198(1)	39(1)
C1	4673(4)	4606(7)	1112(6)	38(2)
N2	4256(3)	3683(9)	940(6)	50(2)
C3	3724(4)	4153(13)	671(9)	57(3)
C4	3594(5)	5545(11)	638(9)	60(3)
C5	4051(6)	6450(12)	809(10)	69(3)
C6	4592(4)	5986(9)	1055(8)	51(2)
N21	5232(3)	4007(7)	1381(5)	37(1)
N22	5713(3)	4773(6)	1574(6)	42(2)
C23	6126(4)	3859(8)	1781(7)	42(2)
N24	5927(3)	2534(7)	1748(5)	37(1)
C25	5365(4)	2679(8)	1491(7)	42(2)
C7	6741(5)	4252(12)	2056(10)	56(3)
C13	5939(5)	253(10)	3183(9)	53(3)
O13	5688(5)	31(12)	3742(9)	89(4)
C14	7047(4)	1328(10)	3301(8)	54(2)
O14	7437(4)	1653(12)	3971(7)	90(3)
C10	6756(4)	−1323(10)	2623(9)	55(3)
O10	6971(4)	−2361(8)	2875(9)	87(3)
C11	6808(5)	675(11)	1153(9)	54(3)
O11	7044(5)	721(11)	561(9)	87(4)
C12	5741(4)	−564(9)	1156(9)	47(2)
O12	5396(4)	−1246(10)	637(7)	78(3)

$^aU_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

dyltriazole ligand compared to a carbon monoxide ligand. The C–O distances are also in the range expected with an average value of 1.14 Å. One of the C–O distances *cis* to the W–triazole bond is somewhat longer at 1.150(13) Å but this is not significant. All bond lengths in the ligand are as expected, and the pyridyl and triazole ring systems are essentially coplanar. As is normally found in triazole compounds the bond lengths in the triazole ring are not identical with the slightly short N22–C23 and N24–C25 vectors indicating the formal location of the double bonds in the ring.

Conclusions

The structural characterisation of $W(CO)_5$-(3Metrpy) indicates that, in the Uhlmann condensation used to prepare the ligand, the pyridine group is bound to the triazole ring through the nitrogen atom which is furthest from the methyl substitutent. It would seen that in the formation of both the ligand and the metal complex, steric factors are important and the ligand coordinates to the metal centre via the least sterically hindered nitrogen. In this instance, the mode of coordination precludes the complex undergoing further intramolecular rearrangements to produce the chelate product.

TABLE 3. $W(CO)_5$(Metrpy) interatomic distances (Å) and angles (°)

N24–W	2.273(7)
C13–W	2.013(11)
C14–W	2.017(10)
C10–W	1.974(10)
C11–W	2.037(10)
C12–W	2.039(10)
N2–C1	1.325(12)
C6–C1	1.351(11)
N21–C1	1.427(10)
C3–N2	1.321(12)
C4–C3	1.383(15)
C5–C4	1.385(18)
C6–C5	1.341(15)
N22–N21	1.347(10)
C25–N21	1.324(10)
C23–N22	1.309(11)
N24–C23	1.370(10)
C7–C23	1.484(13)
C25–N24	1.319(10)
O13–C13	1.150(13)
O14–C14	1.146(13)
O10–C10	1.138(12)
O11–C11	1.144(14)
O12–C12	1.133(12)
C13–W–N24	87.3(3)
C14–W–N24	93.5(3)
C14–W–C13	90.8(5)
C10–W–N24	177.2(3)
C10–W–C13	90.0(4)
C10–W–C14	87.1(4)
C11–W–N24	92.6(4)
C11–W–C13	177.5(4)
C11–W–C14	91.7(5)
C11–W–C10	90.1(4)
C12–W–N24	92.1(3)
C12–W–C13	87.5(5)
C12–W–C14	174.1(4)
C12–W–C10	87.2(4)
C12–W–C11	90.0(4)
C6–C1–N2	124.5(8)
N21–C1–N2	113.5(7)
N21–C1–C6	122.0(8)
C3–N2–C1	117.3(9)
C4–C3–N2	122.8(11)
C5–C4–C3	116.6(10)
C6–C5–C4	121.0(10)
C5–C6–C1	117.6(10)
N22–N21–C1	122.5(7)
C25–N21–C1	127.3(7)
C25–N21–N22	110.2(7)
C23–N22–N21	103.9(6)
N24–C23–N22	112.5(7)
C7–C23–N22	122.5(8)
C7–C23–N24	125.0(8)
C23–N24–W	132.1(5)
C25–N24–W	123.5(5)
C25–N24–C23	104.0(6)
N24–C25–N21	109.4(7)
O13–C13–W	175.6(10)
O14–C14–W	171.9(10)
O10–C10–W	179.6(8)
O11–C11–W	176.9(10)
O12–C12–W	173.7(9)

Supplementary material

Thermal vibration parameters and hydrogen coordinates are available from the authors on request.

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