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Complexes of polyhydro-2,2′-bipyridines with molybdenum and tungsten carbonyls

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Abstract

Reduction of 2,2′-bipyridine with tin in hydrochloric acid produces both 2-(2′-piperidinyl) pyridine and (1,2,3,6-tetrahydro)-2,2′-bipyridine, which have been characterised by (IR, NMR, and UV) spectroscopy. Tetracarbonyl–molybdenum and –tungsten complexes of these ligands exhibit a solvatochromic behaviour very similar to that of the analogous 2,2′-bipyridine complexes.

Key words: Molybdenum; Tungsten; Solvatochromism; Charge transfer; Electronic; Bipyridine

1. Introduction

The observation that the electronic absorption spectrum of $[Mo(CO)_4(bipy)]$ (bipy denotes 2,2′-bipyridine) in solution in the visible region is sensitive to the solvent used was reported 25 years ago [1]. The solvent-sensitive absorption is assigned to a metal-to-ligand charge transfer (MLCT) transition. There have been many subsequent investigations of this phenomenon which have involved both various metals and a great range of ligands. The subject has been reviewed recently [2]. In general, it is observed that the energy of the lower of (usually) two MLCT absorptions increases as the polarity of the solvent increases. Whereas $[Mo(CO)_4(bipy)]$ exhibits solvatochromism, *cis*-$[Mo(CO)_4(pyr)_2]$ (pyr is pyridine) does not do so, from which it is concluded that the conjugated character of the heteroaromatic bidentate bipy ligand is intrinsic to the observation. Recently, determinations of the structures of the benzene solvate complexes $[Mo(CO)_4(3,3'\text{-}Me_2\text{-}2\text{-}2'\text{-bipy}) \cdot C_6H_6]$ [3] and $[Mo(CO)_4(6,6'\text{-}Me_2\text{-}2\text{-}2'\text{-bipy}) \cdot C_6H_6]$ [4] have shown that the solvent molecule is beyond Van der Waals contact with the heterocyclic ligand molecule in each of these complexes. The visible absorption spectra of each of these complexes exhibit solvatochromism [5]. The structures also show that the bipyridine ligands are significantly distorted by non-bonding steric repulsion, whether intra-ligand (CH_3/CH_3) as in $[Mo(CO)_4(3,3'\text{-}Me_2\text{-}2,2'\text{-bipy}) \cdot C_6H_6]$, or inter-ligand ($CH_3/CO$) as in $[Mo(CO)_4(6,6'\text{-}Me_2\text{-}2,2'\text{-bipy})C_6H_6]$. The importance of steric factors in the solute as an influence on the solvatochromic behaviour of diazabuta-1,3-diene complexes was recognised early [6]. We have prepared 2-(2′-piperidinyl)pyridine and its simple complexes with molybdenum(0) and tungsten(0) in order to explore further the influence of structural factors on solvatochromism.

2. Results and discussion

2.1. Ligand synthesis

The compound 2-(2′-piperidinyl)pyridine, **1**, was first reported as the product of reduction of bipy by tin in hydrochloric acid [7]. The yield was not recorded. The same product is obtained by reduction of bipy with nickel–aluminium alloy in aqueous alkali [8], with potassium metal THF [9], with zinc dust in alkaline ethanol [10], or electrochemically at a dropping mercury electrode in alkaline solution [11]. It should be noted that the potassium metal reduction of bipy also produces (3,4,5,6-tetrahydro)-2,2′-bipyridine [9]. The coordination chemistry of **1**, a chiral bidentate ligand,

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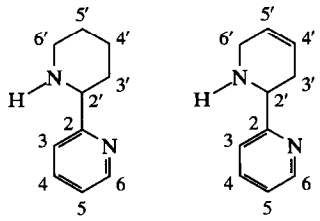

1 2

Scheme 1.

has hardly been investigated. The stability constants of a copper(II) complex of **1** have been reported [12]. These authors also recorded an amazing 70% yield of **1** from the reduction of bipy by tin in hydrochloric acid [12]. We have found that thin-layer chromatography of the liquid product of this reaction indicates that it is a mixture.

Column chromatography of the liquid product on silica with methanol/diethyl ether/water (8:2:1 by volume) as solvent enables the separation of residual bipy from 2-(2'-piperidinyl)pyridine, **1**, and 1',2',3'6'-tetrahydro-2,2'bipyridine, **2**. In a typical reaction, conversion of bipy was 60%, and the yield of **1** was 10% and that of **2** was 5%. Both **1** and **2** are liquids that may be separated as their bishydrochlorides. The enantiomers of **1** and **2** were not separated. The free bases are sensitive to aerial oxidation. Details of the characterisation of **1** and **2** are given in Section 3. The ^1H and ^{13}C NMR spectra serve to distinguish the olefin, **2**, from the substituted pyridine, **1** and to establish their structures.

2.2. Complexes and their characterisation.

Both compounds **1** and **2** (as racemic mixtures) react at room temperature in THF solution with $[Mo(CO)_4$-(bicyclo[2.2.1]hepta-1,4-diene)] to form molybdenum complexes **3** and **4** respectively, and with $[W(CO)_4$-$(piperidine)_2]$ to form tungsten complexes **5** and **6** respectively, with satisfactory yields that were not optimised. These complexes are isolated as red-brown solids which decompose at temperatures above *ca.* 120°C. The complexes were satisfactorily characterised by microanalysis and spectroscopy (IR and ^1H, ^{13}C NMR). Assignment of the ^1H NMR spectra was made on the basis of coupling constant measurements as far as possible. Comparison of these results with those for bipy and $[M(CO)_4(bipy)]$ (M = Mo, W) shows that the coordination shifts are in accord with expectation, being particularly large for those carbon atoms (C2, C2', C6, C6') that are adjacent to the donor atoms.

The visible absorption spectra of all four complexes were recorded in five solvents of different polarity. We have used the index of polarity, E_{MLCT} that was developed by Manuta and Lees [13] and is based on the solvatochromism of $[W(CO)_4(bipy)]$ and is, in turn, related to the π^* index of Kamlet and Taft [14]. The results (Table 1) show that all of the complexes are solvatochromic and that their behaviour is quite similar to that of $[M(CO)_4(bipy)]$ (M = Mo,W) in this respect. This implies that conjugation between the donor atoms in a bidentate ligand is not necessary for observation of solvatochromism. The implications of this result for a coherent understanding of the solvatochromism of compounds of this type will be considered in detail later. There is no clear evidence from molecular modelling for piperidinyl/CO interligand steric repulsion. However the heterocycle is not constrained so that such repulsive interactions are avoidable; therefore, we must conclude that interligand intramolecular interaction of the type found [4] in $[Mo(CO)_4(6,6\text{-}Me_2\text{-}2,2'$-bipy)] is insignificant in these complexes.

3. Experimental details

2,2'-Bipyridine and the hexacarbonylmetal compounds were purchased from Aldrich. IR spectra were recorded for liquid films or Nujol mulls between sodium chloride plates on a PE1420 spectrometer. Electronic absorption spectra were recorded for solutions of samples in 1 cm cells on a PU 8740 spectrometer. Proton and ^{13}C NMR spectra were recorded for solutions on a Jeol GX270 FT spectrometer at 270 MHz for ^1H and 67.80 MHz for ^{13}C resonances; δ values in ppm rela-

TABLE 1. Lowest energy MLCT absorption (λ_{max} (nm) in $[M(CO)_4(L\text{–}L)]$ complexes in solution

L–L		Mo			W		
		bipy	1	2	bipy	1	2
Solvent	E_{MLCT} [13]						
Toluene	0.3	497	500	500	518	520	520
$CHCl_3$	0.42	487	485	490	505	500	495
THF	0.59	472	470	465	488	480	485
Acetone	0.82	454	460	455	466	467	452
MeCN	0.98	445	455	450	450	445	455

tive to internal Me_4Si, J values in Hz. Solvents were dried, deaerated and distilled prior to use. All manipulations involving purified ligands and metal carbonyl complexes were carried out in Schlenk-type apparatus under deoxygenated dinitrogen and solutions were protected from daylight.

3.1. Reduction of 2,2'-bipyridine with tin in hydrochloric acid

Tin powder (15.05 g, 126.8 mmol) was added to 2,2'-bipyridine (5.0 g, 32 mmol) dissolved in ethanol (20 ml) hydrochloric acid (200 ml. of 15 per cent solution) was added to the heated (80°C) and vigorously-stirred mixture and eventually all the tin dissolved. (*ca.* 3 h). The hydrogen chloride was allowed to evaporate off in a well-ventilated fume chamber, and then the solution was made alkaline (pH ~ 14) by addition of aqueous sodium hydroxide. The alkaline solution was concentrated by gentle warming. Extraction of the residue with boiling ethanol, filtration, concentration and partition of the residue between water and diethyl ether, provided an ethereal extract which was dried ($MgSO_4$) and then concentrated to leave a yellow-brown oil (1.1 g). The oil was separated by chromatography on silica using a solvent mixture (methanol/diethylether/water (8:2:1 v/v)) into three components: 2-(2-piperidinyl) pyridine, **1**, (0.14 g., 8.9 mmol; R_f 0.25), 1',2',3',6'-tetrahydro-2,2'-bipyridine, **2**, (0.095 g, 5.9 mmol; R_f 0.40) and unreacted 2,2'-bipyridine (0.4 g). The olefin, **2**, slowly oxidised in air so that it was usually converted into the (solid) bishydrochloride, m.pt. 217–218°C. The corresponding bis-hydrochloride **1** · 2HCl had m.pt. 195–196°C (lit. [7] 196–197°C).

3.2. 2-(2'-piperidinyl)pyridine, 1

B.p. 115°/0.3 torr. Found: C, 74.0; H, 8.5; N, 16.8. $C_{10}H_{14}N_2$ requires C, 74.0; H, 8.7; N 17.2%. $\delta_H(CDCl_3)$ 8.51 (1H, dd, H6, J 4.9, 0.9), 7.62 (1H, td, H3, J 7.4, 1.9), 7.32 (1H, d, H4, J 7.7), 7.12 (1H, dd, H5, J 7.1, 4.9), 3.46 (2H, dd, H6', J 2.7, 10.2, 146.6 (gem)), 2.79 (1H, td, H2', J 2.9, 11.3), 2.59 (1H, s, N*H*), 1.92 (2H, m, H3'), 1.53 (4H, m, H5', H4'). $\delta_c(CDCl_3)$ 163.47 (C2), 148.99 (C6), 136.59 (C4), 121.96 (C5), 120.53 (C3), 62.47 (C2'), 47.18 (C6'), 33.13 (C3'), 26.09 (C5'), 25.04 (C4'), m/z (%) (CI–NH_3): 163 ($M^+ + 1$) (100). IR (film) 3280, 3040, 2930, 2850, 1590, 1570, 1470, 1430, 1110, 750, 660 cm^{-1}. UV/vis (hexane) $\lambda_{max}(\log \epsilon)$ 262 (3.415), 234 (3.361) nm.

3.3. 1',2',3'6'-tetrahydro-2,2'-bipyridine, 2

Found C, 75.3; H, 7.9; N, 17.3. $C_{10}H_{12}N_2$ requires C, 75.0; H, 7.6; N, 17.4%. δ_H ($CDCl_3$) 8.56 (1H, dd, H6, J 4.9, 0.8), 7.66 (1H, td, H3, J 7.7, 1.9), 7.34 (1H, d, H4, J 7.7), 7.18 (1H, dd, H5, J 4.9, 1.6), 5.88 (1H, ddd, H4', J 10.2, 4.4), 5.78 (1H, ddd, H5', J 10.2, 3.7), 3.98 (1H, dd, H2', J 8.6(anti), 5.6(syn)), 3.54 (2H, ddd, H6', J 35.9 (gem), 3.7, 2.2), 2.64 (1H, s, N*H*), 2.35 (2H, m, H3'). δ_c ($CDCl_3$) 162.79 (C2), 149.15 (C6), 136.6 (C4), 126.69 (C4'), 125.14 (C5'), 122.07 (C5), 120.72 (C3), 57.88 (C2'), 45.57 (C6'), 31.84 (C3'). m/z (%) (CI–NH_3): 161 ($M^+ + 1$) (100). IR (film) 3270, 3020, 2910, 2830, 1590, 1565, 1470, 1430, 775, 750, cm^{-1}. UV/vis (hexane) $\lambda_{max}(\log \epsilon)$ 266 (3.43), 260 (3.47), 244 (3.38) nm.

3.4. Tetracarbonyl (2-(2'-piperidinyl)pyridine)molybdenum, 3

The ligand **1** (0.13 g, 0.80 mmol) in THF (1 ml) was added to a solution of $[Mo(CO)_4(\eta^2,\eta^2\text{-}C_7H_8)]$ [15], **7**, (0.31 g, 1.04 mmol) in THF (5 ml) at room temperature. The mixture was stirred in the dark under dinitrogen for one week. The volatiles were removed under vacuum. The residue was redissolved in the minimum amount of THF, the solution was filtered; and finally petroleum ether was added. The crystalline complex separated slowly at 260 K, and the mother liquor was then removed and the solid complex dried under vacuum. Pale red-brown product **3** (0.24 g). Found C, 43.3; H, 3.5; N, 7.1. $C_{14}H_{14}MoN_2O_4$ requires C, 45.4; H, 3.8; N, 7.6%. $\delta_H(CDCl_3)$ 8.87 (1H, dd, H6, J 3.0, 0.6), 7.82 (1H, td, H3, J 8.0, 1.6), 7.31 (1H, d, H4, J 6.0), 7.28 (1H, dd, H5, J 3.0, 1.1), 3.33 (2H, dd, H6', J 140, 10, 2), 2.80–1.0 (8H). δ_c ($CDCl_3$) 222.70, 221.92 (CO_{ax}), 208.01, 206.14 (CO_{eq}) 160.98 (C2), 153.13 (C6), 137.77 (C4), 123.35 (C5), 120.79 (C3), 66.48 (C2'), 54.82 (C6'), 29.81 (C3'), 27.13 (C5'), 23.27 (C4'). IR (Nujol): ν(CO) 2010, 1898, 1871 cm^{-1}.

3.5. Tetracarbonyl (1',2',3',6'-tetrahydro-2,2'-bipyridine)-molybdenum, 4

The procedure outlined above was used, starting from the ligand **2** (0.13 g, 0.8 mmol) and a solution of **7** (0.29 g, 0.97 mmol). Deep red-brown solid product, **4** (0.19 g). Found C, 46.3; H, 3.6; N, 7.3. $C_{14}H_{12}MoN_2O_4$ requires C, 45.7; H, 3.3; N, 7.6%. δ_H ($CDCl_3$) 8.87 (1H, dd, H6), 7.82 (1H, td, H3), 7.31 (1H, d, H4), 7.28 (1H, dd, H5), 5.99 (1H, m, H4'), 5.84 (1H, m, H5'), 4.01 (2H, m, H2'), 3.80 (1H, m, H6'), 2.85 (2H, m, H3'), 2.82 (1H, s, N*H*). δ_c ($CDCl_3$) 222.51, 221.78 (CO_{ax}), 207.59, 205.96 (CO_{eq}), 161.06 (C2) 152.82 (C6), 137.93 (C4), 127.08 (C4'), 123.64 (C5'), 123.53 (C5), 121.24 (C3), 62.34 (C2'), 53.53 (C6'), 29.08 (C3'). IR (Nujol): ν(CO) 2005, 1900, 1865, 1842 cm^{-1}.

3.6. Tetracarbonyl (2-(2'-piperidinyl)pyridine)tungsten, 5

The procedure outlined above was used, starting from the ligand **1** (0.09 g, 0.56 mmol) and a solution of tetracarbonylbis(piperidine)tungsten, **8** (0.30 g, 0.65

mmol). Pale red-brown solid product, **5** (0.11 g). Found C, 35.8; H, 3.8; N, 5.9. $C_{14}H_{14}N_2O_4W$ requires C, 36.7; H, 3.1; N 6.1%. δ_H ($CDCl_3$) 9.02 (1H, dd, H6, *J* 4.0, 0.8), 7.83 (1H, td, H3, *J* 8.1, 1.9), 7.34 (1H, d, H4, *J* 7.0), 7.26 (1H, dd, H5, *J* 3.0, 1.0), 3.51 (2H, dd, H6', *J* 130, 8, 2), 2.9–1.0 (8H). δ_c($CDCl_3$) 215.50, 213.12 (CO_{ax}), 207.35, 203.50 (CO_{eq}), 164.05 (C2), 153.54 (C6), 137.64 (C4), 123.72 (C5), 120.98 (C3), 68.03 (C2'), 55.69 (C6'), 30.02 (C3'), 27.38 (C5'), 22.96 (C4'). IR (Nujol): ν(CO) 2000, 1897, 1870, 1823 cm^{-1}.

3.7. Tetracarbonyl (1',2',3',6'-tetrahydro-2,2'-bipyridine)-tungsten, 6

The procedure outlined above, was used, starting from the ligand **2** (0.09 g, 0.56 mmol) and a solution of **8** (0.301 g, 0.65 mmol). Pale brown solid product, **6** (0.23 g). Found C, 36.1; H, 3.2; N, 6.5. $C_{14}H_{12}N_2O_4W$ requires C, 36.9; H, 2.7; N, 6.1%. δ_H($CDCl_3$) 9.01 (1H, dd, H6), 7.84 (1H, td, H3), 7.34 (1H, d, H4), 7.32 (1H, dd, H5), 5.97 (1H, m, H4') 5.75 (1H, m, H5'), 3.99 (2H, m, H2'), 3.55 (1H, m, H6'), 2.90–2.60 (3H). δ_c($CDCl_3$) 214.77, 213.65 (CO_{ax}), 203.29, 201.08 (CO_{eq}), 161.64 (C2), 153.09 (C6), 137.14 (C4), 127.33 (C4'), 123.79 (C5'). 123.30 (C5), 120.81 (C3), 63.88 (C2'), 54.54 (C6'), 29.31 (C3'). IR (Nujol): ν(CO) 1997, 1921, 1863, 1850 cm^{-1}.

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