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Some new water-soluble zero-valent tetracarbonyl complexes of molybdenum and tungsten containing carboxylate and sulfonate substituted pyridine ligands

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Abstract—Reaction of $[Mo(CO)_6]$ with 2 equiv. of L [L = $3\text{-}NaO_2CC_5H_4N$, $4\text{-}NaO_2CC_5H_4N$, $3,4\text{-}(NaO_2C)_2C_5H_3N$, $3,5\text{-}(NaO_2C)_2C_5H_3N$ or $3\text{-}NaO_3SC_5H_4N$] in a 1 : 1 mixture of refluxing toluene and ethanol gave the water soluble bis(ligand) substituted complexes *cis*-$[Mo(CO)_4L_2]$ (**1**–**5**). Treatment of *cis*-$[W(CO)_4(pip)_2]$ (pip = piperidine) with 2 equiv. of L [L = $3\text{-}NaO_2CC_5H_4N$, $4\text{-}NaO_2CC_5H_4N$, $3,4\text{-}(NaO_2C)_2C_5H_3N$, $3,5\text{-}(NaO_2C)_2C_5H_3N$ or $3\text{-}NaO_3SC_5H_4N$] in a 1 : 1 mixture of toluene and ethanol at room temperature gave the totally water soluble complexes *cis*-$[W(CO)_4L_2]$ (**6**–**10**). © 1997 Elsevier Science Ltd

Keywords: water-soluble; molybdenum(O); tungsten(O); submitted pyridine ligands.

Water-soluble organometallic compounds have become increasingly important in catalytic processes [1,2]. Hitherto, very few zero-valent molybdenum and tungsten complexes of this type have been reported. For example, in 1991 Darensbourg *et al.* [3] described the synthesis and characterization of $[W(CO)_5\{P(C_6H_4SO_3Na\text{-}3)_3\}]$, which contains the water soluble phosphine ligand sodium 3-(diphenylphosphino)benzene sulfonate [4]. In 1993 Darensbourg and Bischoff [5] also described the preparation of the molybdenum complex $[Mo(CO)_5\{P(C_6H_4SO_3\text{-}Na)_3\}]$ and the water soluble bis(ligand) complexes *cis*-$[M(CO)_4\{P(C_6H_4SO_3\text{-}Na)_3\}_2]$ (M = Mo, W). In view of the difficulties of preparing water-soluble phosphines [6] we have been using the carboxylate and sulfonate substituted pyridines to prepare the first examples of seven-coordinate water soluble complexes of molybdenum(II) and tungsten(II) [7].

In this paper we describe the synthesis and characterization of a series of 10 water-soluble zero-valent six-coordinate complexes of the type *cis*-$[M(CO)_4L_2]$ [M = Mo or W; L = $3\text{-}NaO_2CC_5H_4N$, $4\text{-}NaO_2CC_5H_4N$, $3,4\text{-}(NaO_2C)_2C_5H_3N$, $3,5\text{-}(NaO_2C)_2C_5H_3N$ or $3\text{-}NaO_3SC_5H_4N$], which contain the substituted pyridine ligands shown in Fig. 1.

EXPERIMENTAL

The reactions described in this paper were carried out using vacuum/Schlenk line techniques. The complex *cis*-$[W(CO)_4(pip)_2]$ (pip = piperidine) was prepared by the published method [8]. All chemicals were purchased from commercial sources.

Elemental analyses (C, H and N) were determined using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). The IR spectra were recorded on a Perkin–Elmer 1600 FT IR spectrophotometer. The ^1H NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer and referenced to $SiMe_4$.

Cis-$[Mo(CO)_4(3\text{-}NaO_2CC_5H_4N)_2]$ (**1**)

To $[Mo(CO)_6]$ (0.5 g, 1.893 mmol) dissolved in a 1 : 1 mixture of toluene and ethanol (50 cm^3) with continuous stirring was added $3\text{-}NaO_2CC_5H_4N$ (0.54 g, 3.788 mmol). After the solution was refluxed for 24 h, filtered and solvent removed *in vacuo* the pure

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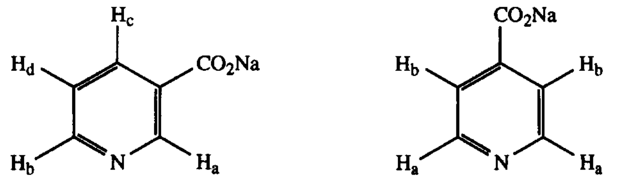
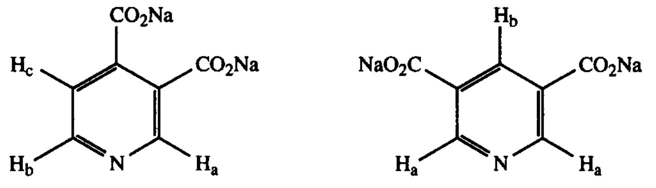


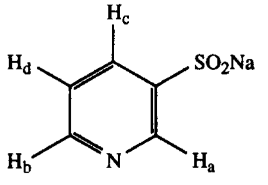
Pyridine-3-carboxylic Acid, sodium salt

Pyridine-4-carboxylic Acid, sodium salt



Pyridine-3,4-dicarboxylic Acid, disodium salt

Pyridine-3,5-dicarboxylic Acid, disodium salt



Pyridine-4-sulfonic Acid, sodium salt

Figure 1. Structures and ^{1}H NMR proton assignments for the carboxylate and sulfonate substituted pyridine ligands, L

product *cis*-$[Mo(CO)_4(3\text{-}NaO_2CC_5H_4N)_2]$ **(1)** was isolated (yield = 0.63 g, 67%).

Similar reactions of $[Mo(CO)_6]$ with 2 equiv. of L [L = $4\text{-}NaO_2CC_5H_4N$, $3,4\text{-}(NaO_2C)_2C_5H_3N$, $3,5\text{-}(NaO_2C)_2C_5H_3N$ or $3\text{-}NaO_3SC_5H_4N$] in a 1 : 1 mixture of refluxing toluene and ethanol for 24 h gave the complexes *cis*-$[Mo(CO)_4L_2]$ **(2–5)**.

Cis-$[W(CO)_4(3\text{-}NaO_2CC_5H_4N)_2]$ **(6)**

To *cis*-$[W(CO)_4(pip)_2]$ (0.5 g, 1.073 mmol) dissolved in a 1 : 1 mixture of toluene and ethanol (50 cm^3) with continuous stirring was added $3\text{-}NaO_2CC_5H_4N$ (0.31 g, 2.146 mmol). After the solution was stirred for 24 h, the reaction mixture was filtered and solvent removed *in vacuo* to give the pure product *cis*-$[W(CO)_4(3\text{-}NaO_2CC_5H_4N)_2]$, **6** (yield = 0.52 g, 83%).

Similar reactions of *cis*-$[W(CO)_4(pip)_2]$ with 2 equiv. of L [L = $4\text{-}NaO_2CC_5H_4N$, $3,4\text{-}(NaO_2C)_2C_5H_3N$, $3,5\text{-}(NaO_2C)_2C_5H_3N$ or $3\text{-}NaO_3SC_5H_4N$] in a 1 : 1 mixture of toluene and ethanol at room temperature for 24 h gave the complexes *cis*-$[W(CO)_4L_2]$ **(7–10)**.

RESULTS AND DISCUSSION

The reaction of $[Mo(CO)_6]$ with 2 equiv. of L [L = $3\text{-}NaO_2CC_5H_4N$, $4\text{-}NaO_2CC_5H_4N$, $3,4\text{-}(NaO_2C)_2C_5H_3N$, $3,5\text{-}(NaO_2C)_2C_5H_3N$ or $3\text{-}NaO_3SC_5H_4N$] in a 1 : 1 mixture of refluxing toluene and ethanol for 24 h affords the new zero-valent complexes *cis*-$[Mo(CO)_4L_2]$ **(1–5)**. The complexes were fully characterized by elemental analysis (C, H and N; Table 1), IR spectroscopy (Table 2) and ^{1}H NMR spectroscopy (Table 3). The complexes are air-stable when in the solid state, but less stable in solution. The complexes are insoluble in methanol, dichloromethane and acetone, but are totally soluble in water.

Complexes **1–5** showed four carbonyl stretching frequencies in their IR spectra in the region 1870–2074 cm^{-1}, which indicates that the complexes, as expected, have the substituted pyridine ligands *cis* to each other. For example, complex **1** shows four carbonyl stretching bands at 2072, 1985, 1935 and 1901 cm^{-1}. A carbonyl (C=O) stretching band was also observed in the IR spectra at approximately 1730 cm^{-1} for complexes **1–4**, whereas the complex *cis*-$[Mo(CO)_4(3\text{-}NaSO_3C_5H_4N)_2]$ **(5)** has an (S=O) stretch at 1219 cm^{-1}. Several unsuccessful attempts were made to grow suitable single crystals for X-ray crystallography of complexes **1–5**, however, it is very likely the structure of **1–5** will be with *cis*-ligands as shown in Fig. 2.

The ^{1}H NMR spectra of the complexes **1–5** were recorded in D_2O. The proton assignments are given on the ligands in Fig. 1. For example, the ^{1}H NMR

Table 1. Physical and analytical data[a] for the complexes *cis*-[M(CO)$_4$L$_2$] (**1**–**10**)

Complex	Yield (%)	Colour	C(%)	H(%)	N(%)
1, *cis*-[Mo(CO)$_4$(3-NaO$_2$CC$_5$H$_4$N)$_2$]	67	Brown	37.8 (38.6)	2.2 (1.6)	5.3 (5.6)
2, *cis*-[Mo(CO)$_4$(4-NaO$_2$CC$_5$H$_4$N)$_2$]	75	Brown	38.2 (38.6)	1.4 (1.6)	5.4 (5.6)
3, *cis*-[Mo(CO)$_4${3,4-(NaO$_2$C)$_2$C$_5$H$_3$N}$_2$]	58	Orange	33.5 (34.3)	1.7 (1.0)	4.4 (4.5)
4, *cis*-[Mo(CO)$_4${3,5-(NaO$_2$C)$_2$C$_5$H$_3$N}$_2$]	71	Orange	35.3 (34.3)	1.3 (1.0)	4.8 (4.5)
5, *cis*-[Mo(CO)$_4$(3-NaO$_3$SC$_5$H$_4$N)$_2$]	64	Red	28.8 (29.5)	2.1 (1.4)	4.5 (4.9)
6, *cis*-[W(CO)$_4$(3-NaO$_2$CC$_5$H$_4$N)$_2$]	83	Red	33.2 (32.8)	1.6 (1.4)	4.5 (4.8)
7, *cis*-[W(CO)$_4$(4-NaO$_2$CC$_5$H$_4$N)$_2$]	79	Red	32.4 (32.8)	1.9 (1.4)	5.4 (4.8)
8, *cis*-[W(CO)$_4${3,4-(NaO$_2$C)$_2$C$_5$H$_3$N}$_2$]	60	Black	29.2 (30.1)	1.2 (0.9)	3.9 (3.9)
9, *cis*-[W(CO)$_4${3,5-(NaO$_2$C)$_2$C$_5$H$_3$N}$_2$]	67	Orange	30.0 (30.1)	0.8 (0.9)	4.6 (3.9)
10, *cis*-[W(CO)$_4$(3-NaO$_3$SC$_5$H$_4$N)$_2$]	71	Red	25.8 (25.5)	1.6 (1.2)	3.9 (4.3)

[a] Calculated values in parentheses.

Table 2. IR data for the complexes *cis*-[M(CO)$_4$L$_2$] (**1**–**10**)[a,b]

Complex	ν(C≡O) (cm^{-1})	ν(C=O)/ ν(S=O) (cm^{-1})
1	2072 (w), 1985 (w), 1935 (m), 1901 (sh)	1712 (s)
2	2074 (m), 2015 (s), 1984 (sh), 1890 (s)	1734 (s)
3	2068 (w), 2014 (w), 1992 (sh), 1899 (s)	1725 (s)
4	2028 (w), 1972 (s), 1955 (s), 1870 (sh)	1714 (s)
5	2066 (m), 1994 (s), 1919 (s), 1899 (sh)	1219 (m)[b]
6	2029 (w), 2005 (m), 1935 (sh), 1880 (s)	1744 (s)
7	2073 (m), 1980 (s), 1964 (sh), 1900 (s)	1732 (s)
8	2074 (s), 1984 (s), 1916 (s), 1874 (s)	1708 (sh)
9	2072 (w), 1978 (m), 1920 (m), 1895 (m)	1738 (s)
10	2070 (m), 2003 (sh), 1947 (m), 1872 (s)	1232 (s)[b]

[a] Spectra measured as KBr discs.
[b] ν(S=O) stretching frequency.

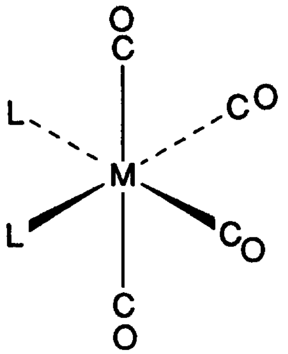


Figure 2. Proposed structure for the six-coordinate complexes *cis*-[M(CO)$_4$L$_2$] (M = Mo or W; L = substituted pyridine).

Table 3. ^{1}H NMR data for the complexes *cis*-[M(CO)$_4$L$_2$] (**1**–**10**)[a]

Complex	^{1}H NMR (δ) ppm
1	8.8 (s, 2H$_a$, 3-NaO$_2$CC$_5$H$_4$N), 8.4 (d, J = 6.3 Hz, 2H$_b$, 3-NaO$_2$CC$_5$H$_4$N), 8.1 (d, J = 7.6 Hz, 2H$_c$, 3-NaO$_2$CC$_5$H$_4$N), 7.3 (m, 2H$_d$, 3-NaO$_2$CC$_5$H$_4$N)
2	8.4 (d, J = 7.1 Hz, 4H$_a$, 4-NaO$_2$CC$_5$H$_4$N), 7.5 (d, J = 7.1 Hz, 4H$_b$, 4-NaO$_2$CC$_5$H$_4$N)
3	8.6 [s, 2H$_a$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N], 8.3 [d, J = 7.9 Hz, 2H$_b$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N], 7.2 [d, J = 6.7 Hz, 2H$_c$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N]
4	8.8 [d, J = 1.8 Hz, 2H$_a$, 3,5-(NaO$_2$C)$_2$C$_5$H$_3$N], 7.9 [d, J = 1.8 Hz, 4H$_b$, 3,5-(NaO$_2$C)$_2$C$_5$H$_3$N]
5	9.0 (m, 2H$_a$, 3-NaO$_3$SC$_5$H$_4$N), 8.9 (d, J = 6.9 Hz, 2H$_b$, 3-NaO$_3$SC$_5$H$_4$N), 8.7 (d, J = 7.3 Hz, 2H$_c$, 3-NaO$_3$SC$_5$H$_4$N), 7.4 (s, 2H$_d$, 3-NaO$_3$SC$_5$H$_4$N)
6	9.0 (s, 2H$_a$, 3-NaO$_2$CC$_5$H$_4$N), 8.6 (m, 2H$_b$, 3-NaO$_2$CC$_5$H$_4$N), 8.4 (d, J = 7.9 Hz, 2H$_c$, 3-NaO$_2$CC$_5$H$_4$N), 7.6 (m, 2H$_d$, 3-NaO$_2$CC$_5$H$_4$N)
7	8.7 (d, J = 7.2 Hz, 4H$_a$, 4-NaO$_2$CC$_5$H$_4$N), 7.9 (J = 7.2 Hz, 4H$_b$, 4-NaO$_2$CC$_5$H$_4$N)
8	8.8 [s, 2H$_a$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N], 8.6 [d, 8.2 Hz, 2H$_b$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N], 7.5 [d, J = 7.8 Hz, 2H$_c$, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N]
9	8.6 [d, J = 1.6 Hz, 2H$_a$, 3,5-(NaO$_2$C)$_2$C$_5$H$_3$N], 7.5 [d, J = 1.6 Hz, 4H$_b$, 3,5-(NaO$_2$C)$_2$C$_5$H$_3$N]
10	9.2 (s, 2H$_a$, 3-NaO$_3$SC$_5$H$_4$N), 8.7 (m, 2H$_b$, 3-NaO$_3$SC$_5$H$_4$N), 8.3 (m, 2H$_c$, 3-NaO$_3$SC$_5$H$_4$N), 7.8 (m, 2H$_d$, 3-NaO$_3$SC$_5$H$_4$N)

[a] Spectra recorded in D$_2$O (+25°C) and referenced to SiMe$_4$.

spectrum of *cis*-[Mo(CO)$_4$(3-NaO$_2$CC$_5$H$_4$N)$_2$] (**1**) has two doublet resonances at 8.4 (H$_b$) and 8.1 ppm (H$_c$), a singlet at 8.8 ppm (H$_a$) and a multiplet at 7.3 ppm (H$_d$), all of which can be attributed to the pyridine protons. The complex *cis*-[Mo(CO)$_4$(4-NaO$_2$C-C$_5$H$_4$N)$_2$] (**2**) has resonances at 8.4 (H$_a$) and 7.5 ppm (H$_b$), both of which are doublets. The pyridine protons for complex **3** has three resonances in the ^{1}H NMR spectrum at $\delta = 8.6$ (H$_a$), 8.3 (H$_b$) and 7.2 ppm (H$_c$). The ^{1}H NMR spectrum of **4** has two doublet resonances at 8.8 (H$_a$) and 7.9 ppm (H$_b$). Complex **5** has four resonances in the ^{1}H NMR spectrum at 9.0 (H$_a$), 8.9 (H$_b$), 8.7 (H$_c$) and 7.4 ppm (H$_d$) due to the pyridine protons.

Treatment of *cis*-[W(CO)$_4$(pip)$_2$] (pip = piperidine) with 2 equiv. of L [L = 3-NaO$_2$CC$_5$H$_4$N, 4-NaO$_2$C-C$_5$H$_4$N, 3,4-(NaO$_2$C)$_2$C$_5$H$_3$N, 3,5-(NaO$_2$C)$_2$C$_5$H$_3$N or 3-NaO$_3$SC$_5$H$_4$N] in a 1 : 1 mixture of toluene and ethanol for 24 h yields the new zero-valent complexes *cis*-[W(CO)$_4$L$_2$] (**6**–**10**). The complexes have been characterized by elemental analysis (Table 1), IR spectroscopy (Table 2) and ^{1}H NMR spectroscopy (Table 3). The complexes have very similar stability and solubilities to their molybdenum analogues **1**–**5**.

The IR spectra of complexes **6**–**10** are similar to those of complexes **1**–**5**. Each complex showed four carbonyl stretching bands in the region 2074–1872 cm^{-1}, which suggests that the complexes have *cis*-geometry, as shown in Fig. 2. The complexes **6**–**9** have a single υ(C=O) stretch at approximately 1725 cm^{-1}, whilst the complex **10** has an S=O stretch at 1232 cm^{-1}. The ^{1}H NMR spectra of the complexes **6**–**10** as expected showed similar resonances to the complexes **1**–**5**. Several unsuccessful attempts to grow suitable single crystals for X-ray crystallography were made, however, IR spectroscopy confirms the expected *cis*-stereochemistry as shown in Fig. 2.

In conclusion, we have described a high yield synthesis of ten new water-soluble octahedral complexes of the type *cis*-[M(CO)$_4$L$_2$], which have the commercially available and low-priced carboxylate and sulfonate substituted pyridine ligands which enable the complexes to be soluble in water. We are currently exploring the catalytic activity of these complexes.

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