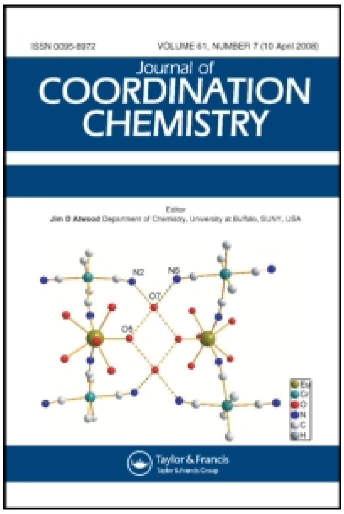

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Group 6 metal carbonyl complexes containing 3,5-dimethyl-4-ferrocenylmethylpyrazole: synthesis, structure and electrochemical properties

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Group 6 metal carbonyl complexes containing 3,5-dimethyl-4-ferrocenylmethylpyrazole: synthesis, structure and electrochemical properties

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Reaction of $M(CO)_6$ with 3,5-dimethyl-4-ferrocenylmethylpyrazole under UV irradiation yields monosubstituted group 6 metal carbonyl complexes $M(CO)_5L$ ($M = Cr$, Mo or W; $L = 3,5$-dimethyl-4-ferrocenylmethylpyrazole). Their electrochemical behaviour, investigated by cyclic voltammetry, indicates that chromium and tungsten complexes exhibit two one-electron *quasi*-reversible couples corresponding to the ferrocenyl group and the chromium or tungsten centre, respectively, while the molybdenum complex has one *quasi*-reversible couple corresponding to the ferrocenyl group and one irreversible oxidation process for molybdenum. The crystal structure of $W(CO)_5L$, determined by X-ray diffraction methods, shows that ferrocenylpyrazole acts as a monodentate ligand, and W is six-coordinate with *quasi*-octahedral coordination geometry. The complex is linked into a one-dimensional chain in the lattice through weak intermolecular hydrogen bonds with metal carbonyls acting as acceptors.

Keywords: Group 6 carbonyl complexes; Ferrocene; Pyrazole; Cyclic voltammetry; Crystal structure

1. Introduction

Ferrocene and its derivatives have been extensively used in many fields [1]. For example, ferrocenyl derivatives are very important electron-transfer systems in molecular electronics due to their characteristic redox behaviour [2] and they may be useful electrochemical probes of electron-transfer processes in biological molecules [3]. Compounds with pyrazole ligands linked to the ferrocenyl fragment have shown interesting electrochemical behaviour and structural features, so there has been increasing interest in the use of ferrocenylpyrazole ligands to produce polymetallic

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species [4–12]. A recent investigation of the reaction of ferrocenylpyrazole with $M(CO)_6$ (M = Cr, Mo or W) shows that substituents at the 3- and 5-positions of the pyrazole ring affect significantly the structures of complexes [13, 14]. In order to understand effects of electronic and steric characteristics of the substituents at the 4-position of the pyrazole ring on reactivity and structural features of complexes, we have studied related species. Here we report the synthesis, structure and electrochemical properties of group 6 metal carbonyl complexes containing 3,5-dimethyl-4-ferrocenylmethylpyrazole.

2. Experimental

2.1. *Physical measurements*

All reactions were carried out under an oxygen-free atmosphere. Solvents were dried by standard methods and distilled prior to use. ^{1}H NMR spectra were recorded on a Bruker AV 300 spectrometer using $CDCl_3$ as solvent. IR spectra were obtained with a Bruker Equinox55 spectrophotometer (KBr pellets or Nujol mulls). Elemental analyses were carried out on a Yanaco CHN Corder MT-3 instrument.

2.2. *Synthesis of $Cr(CO)_5L$ (1)*

The ligand 3,5-dimethyl-4-ferrocenylmethylpyrazole (L) was prepared according to a literature method [15]. ^{1}H NMR: δ 2.26 (s, 6H, CH_3), 3.45 (s, 2H, CH_2), 4.11 (m, 4H, C_5H_4), 4.17 (s, 5H, C_5H_5), 6.47 (br, s, 1H, NH). A solution of $Cr(CO)_6$ (1 mmol) and L (1 mmol) dissolved in THF (30 cm^3) was irradiated with a 300 W high-pressure mercury lamp for 8 h at room temperature. After reaction was complete, solvent was removed *in vacuo*, and the residue purified by column chromatography on silica using CH_2Cl_2/hexane (v : v = 1 : 1) as eluent. The yellow eluent was evaporated to dryness under vacuum, and the residue recrystallized from CH_2Cl_2/hexane to give orange-yellow crystals. Yield: 64%. Anal. Calcd for $C_{21}H_{18}CrFeN_2O_5$ (%): C, 51.85; H, 3.70; N, 5.76. Found: C, 51.68; H, 3.46; N, 5.35. ^{1}H NMR: δ 2.21, 2.28 (s, s, 3H, 3H, CH_3); 3.41 (s, 2H, CH_2); 4.08, 4.16 (m, s, 4H, 5H, FcH); 9.02 (br, s, 1H, NH). IR (Nujol, cm^{-1}): $\nu_{NH} = 3407.9$ (m); $\nu_{CO} = 2069.6$ (w), 1989.1 (s), 1956.1 (vs), 1934.2 (vs), 1846.7 (vs), 1831.8 (vs).

2.3. *Synthesis of $Mo(CO)_5L$ (2)*

The complex was obtained similarly using $Mo(CO)_6$ (1 mmol) instead of $Cr(CO)_6$ as described above for **1**. Yellow crystals, yield: 60%. Anal. Calcd for $C_{21}H_{18}FeMoN_2O_5$ (%): C, 47.55; H, 3.40; N, 5.28. Found: C, 47.21; H, 3.18; N, 5.57. ^{1}H NMR: δ 2.14, 2.19 (s, s, 3H, 3H, CH_3); 3.34 (s, 2H, CH_2); 3.99, 4.07 (m, s, 4H, 5H, FcH); 9.05 (br, s, 1H, NH). IR (Nujol, cm^{-1}): $\nu_{NH} = 3403.6$ (m); $\nu_{CO} = 2075.0$ (w), 1993.5 (sh), 1958.7 (vs), 1938.8 (vs), 1844.6 (vs), 1827.7 (vs).

2.4. *Synthesis of $W(CO)_5L$ (3)*

The complex was obtained similarly using $W(CO)_6$ (1 mmol) instead of $Cr(CO)_6$ as described above for **1**. Orange-yellow crystals, yield: 65%. Anal. Calcd for

Table 1. Crystallographic data for complex **3**.

Formula	$C_{21}H_{18}FeN_2O_5W$
Formula weight	618.07
Crystal size (mm)	0.40 × 0.20 × 0.18
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	10.2630(14)
b (Å)	14.650(2)
c (Å)	14.9098(19)
T (K)	294(2)
V (Å^3)	2241.8(5)
D_{calc} (g cm^{-3})	1.831
2θ Range (°)	3.9–52.72
Absorption coefficient (mm^{-1})	5.807
Z	4
F(000)	1192
Reflections collected	12677
Independent reflections (R_{int})	4583 (0.0487)
No. of parameters	274
Residuals R, Rw [$I > 2\sigma(I)$]	0.0347, 0.0555
Goodness-of-fit	0.989
Absolute structure parameter	0.00(4)
Largest diff. peak and hole (e Å^{-3})	0.642 and −0.615

$C_{21}H_{18}FeN_2O_5W$ (%): C, 40.78; H, 2.91; N, 4.53. Found: C, 40.93; H, 2.93; N, 4.98. ^{1}H NMR: δ 2.16, 2.21 (s, s, 3H, 3H, CH_3); 3.36 (s, 2H, CH_2); 4.01, 4.08 (m, s, 4H, 5H, FcH); 9.08 (br, s, 1H, NH). IR (KBr, cm^{-1}): $\nu_{NH} = 3389$ (m); $\nu_{CO} = 2071$ (w), 1985 (sh), 1950 (s), 1928 (vs), 1858 (s), 1823 (s).

2.5. *Crystal structure determination*

Crystals of complex **3** suitable for X-ray analysis were grown from CH_2Cl_2/hexane at 4°C. Intensity data were collected at 294 K on a Bruker SMART CCD equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the $\theta/2\theta$ scan technique. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. A summary of crystal data is listed in table 1.

2.6. *Electrochemical measurements*

Cyclic voltammetry experiments were performed on a BAS-Epsilon electrochemical analyser equipped with a three-electrode assembly with 0.1 M Bu_4NPF_6 as supporting electrolyte and CH_2Cl_2 as solvent. The working electrode was glassy carbon ($\phi = 3$ mm) and the reference electrode 0.1 M $AgNO_3$/Ag prepared in 0.1 M Bu_4NPF_6-CH_3CN solution. A Pt filament was used as auxiliary electrode. The ferrocenium–ferrocene redox couple was taken as standard. $E_{1/2}$ values were determined as $(E_{pa} + E_{pc})/2$.

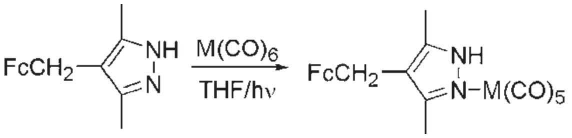
3. Results and discussion

3.1. *Synthesis and properties of the complexes*

Reaction of 3,5-dimethyl-4-ferrocenylmethylpyrazole with $M(CO)_6$ (M = Cr, Mo and W) under UV irradiation in a 1 : 1 mol ratio at room temperature yielded complexes **1–3** (scheme 1). These complexes are stable in the solid state, and solutions of chromium and tungsten complexes can be handled in air without decomposition. The molybdenum complex is slightly air-sensitive in solution. All complexes are soluble in polar solvents such as acetone and chlorinated solvents. Characteristic N–H stretches in complexes **1–3** appear at 3404, 3408 and 3389 cm^{-1}, respectively. Possibly due to superposition of the absorption of the different carbonyl groups due to weak N–H···O interactions, six ν_{CO} bands are observed in complexes **1–3**. The weak ν_{CO} band at ca 2070 cm^{-1} can be assigned to the $A_{1\mathrm{eq}}$ mode for pseudo $C_{4\mathrm{v}}$ symmetry at the metal centre [16]. ^{1}H NMR spectra of complexes **1–3** indicate significant shifts downfield of the N–H proton compared with the free ligand; the N–H signal in the complexes appears at ca 9 ppm, while the corresponding signal in the free ligand appears at 6.47 ppm.

3.2. *Crystal structure of 3*

The molecular structure of complex **3** is shown in figure 1. Selected bond distances and angles are listed in table 2. The tungsten atom is six-coordinate with *quasi*-octahedral coordination geometry. The W–N distance is 2.258(5) Å, slightly longer than that in (3-FcPz)W$(CO)_5$ (Fc = ferrocenyl and Pz = pyrazole, 2.204(8) Å) [13], but similar to those found in other octahedral W(0) complexes with pyrazole ligands (2.258(6) Å in (3-Me-5-FcPz)W$(CO)_5$ [13] and average 2.255 Å in $CH_2(3,5\text{-}Me_2\text{-}4\text{-}ClPz)_2W(CO)_4$ [17]).



Scheme 1. Fc = Ferrocenyl, M = Cr (**1**); Mo (**2**); W (**3**).

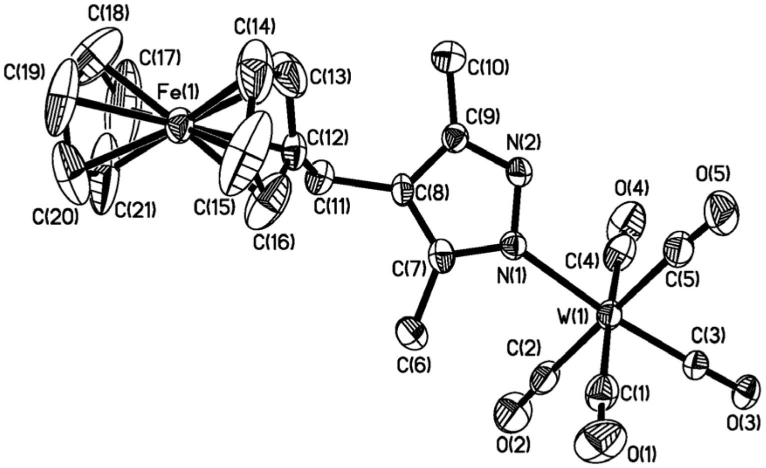


Figure 1. The molecular structure of **3** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for complex **3**.

Bond lengths			
W(1)–C(1)	2.045(9)	O(1)–C(1)	1.124(10)
W(1)–C(2)	2.036(7)	O(2)–C(2)	1.131(7)
W(1)–C(3)	1.960(7)	O(3)–C(3)	1.154(8)
W(1)–C(4)	2.040(10)	O(4)–C(4)	1.131(9)
W(1)–C(5)	2.049(8)	O(5)–C(5)	1.132(7)
W(1)–N(1)	2.258(5)	C(8)–C(11)	1.510(9)
Bond angles			
C(2)–W(1)–C(1)	87.9(4)	C(7)–N(1)–W(1)	136.9(5)
C(3)–W(1)–C(1)	88.5(3)	N(2)–N(1)–W(1)	118.3(4)
C(4)–W(1)–C(1)	173.9(5)	O(1)–C(1)–W(1)	175.8(9)
C(3)–W(1)–C(2)	92.1(4)	O(2)–C(2)–W(1)	177.0(6)
C(2)–W(1)–C(4)	88.7(5)	O(3)–C(3)–W(1)	178.2(8)
C(3)–W(1)–C(4)	86.7(3)	O(4)–C(4)–W(1)	174.8(11)
C(3)–W(1)–C(5)	88.0(4)	O(5)–C(5)–W(1)	177.3(7)
C(2)–W(1)–C(5)	178.5(4)	C(9)–C(8)–C(11)	127.5(6)
C(4)–W(1)–C(5)	92.9(5)	C(7)–C(8)–C(11)	128.1(7)
C(1)–W(1)–C(5)	90.6(4)	C(12)–C(11)–C(8)	114.2(5)
C(1)–W(1)–N(1)	95.7(3)	C(4)–W(1)–N(1)	89.4(3)
C(2)–W(1)–N(1)	91.9(3)	C(5)–W(1)–N(1)	88.1(3)

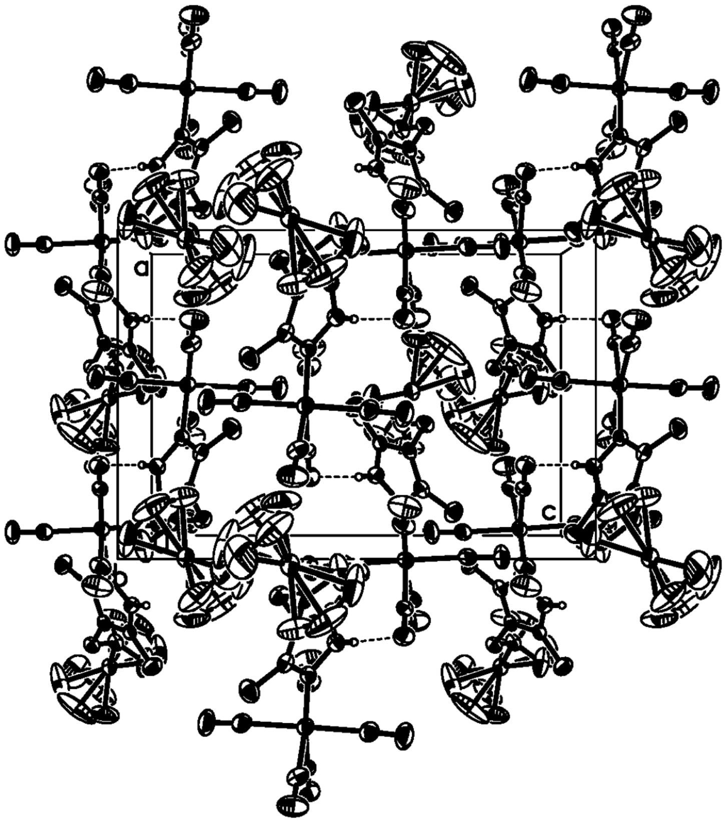


Figure 2. The crystal packing of complex **3** emphasizing hydrogen bonding interactions (N(2)–H···O(3)^{i} = 3.106 Å; symmetry code i is $x-1/2$, $-y+5/2$, $-z+2$).

Table 3. Electrochemical data for ligand L and complexes **1**–**3**.

	E_{pa1} (mV)	E_{pc1} (mV)	$E_{1/2}$ (mV)	E_{pa2} (mV)	E_{pc2} (mV)	$E_{1/2}$ (mV)
L	62	−153	−46			
1	42	−73	−16	400	297	349
2	42	−66	−12	560		
3	56	−86	−15	580	464	522

The W–C distance *trans* to the pyrazole ligand is shorter than the other four W–C distances, while the corresponding C–O distance is longer than the other four C–O distances. In addition, carbonyls *cis* to the pyrazole ligand also deviate from linearity. Owing to the flexible CH_2 spacer, repulsion between the ferrocenyl and pyrazole ligands is less than in (3-FcPz)W$(CO)_5$. Furthermore, cyclopentadienyl rings lie nearly parallel to each other with the dihedral angle (0.2°) being smaller than those in W$(CO)_5$L (L = 3-ferrocenyl or 3(5)-methyl-5(3)-ferrocenylpyrazole) [13].

As is the case with (3-FcPz)W$(CO)_5$, hydrogen bonds formed by metal carbonyls as hydrogen bond acceptors are observed in **3**. The crystal packing (figure 2) shows that the molecules are linked into a one-dimensional chain via weak hydrogen bonds between the N–H groups and the oxygen atoms of metal carbonyls *trans* to pyrazole ligands in adjacent molecules. The hydrogen bond N···O distance is 3.106 Å, and the N–H···O angle is 173.86°.

3.3. *Electrochemical properties*

Measurements were made at room temperature with a scan rate of $100\,\mathrm{mV\,s^{-1}}$. Anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, as well as $E_{1/2} = (E_{pa} + E_{pc})/2$ are listed in table 3. The electrochemical behaviour of the chromium complex **1** is similar to that of Cr$(CO)_5$L (L = 3-ferrocenyl or 3(5)-methyl-5(3)-ferrocenylpyrazole) [13], exhibiting two *quasi*-reversible one-electron oxidation processes for the ferrocenyl group and chromium, respectively. However, an irreversible oxidation process at the molybdenum centre is observed in complex **2**. The low stability of this complex may be responsible for the irreversible oxidation. In addition, the electrochemical behaviour of the tungsten complex **3** is different from that of W$(CO)_5$L (L = substituted pyrazole) [13, 14]. Besides one *quasi*-reversible one-electron oxidation process for the ferrocenyl group, oxidation of tungsten is also *quasi*-reversible. Compared with the free ligand, the redox potential ($E_{1/2}$) of the ferrocenyl group in complexes **1**–**3** is slightly higher, possibly because of inductive effects of the electron-withdrawing M$(CO)_5$ fragments.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 277916 for **3**. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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