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URACIL AND THIOURACIL COMPLEXES OF DICYCLOPENTADIENYL MOLYBDENUM AND TUNGSTEN: PREPARATION AND ELECTROCHEMISTRY. THE STRUCTURES OF $[M(\eta^5\text{-}C_5H_5)_2(2\text{-}SN_2OC_4H_3)][PF_6]$, $[M(\eta^5\text{-}C_5H_5)_2\{2\text{-}S(CH_3)N_2OC_4H_2\}][PF_6]$, $[Mo(\eta^5\text{-}C_5H_5)_2(4\text{-}SN_2OC_4H_3)][PF_6]$ AND $[Mo(\eta^5\text{-}C_5H_5)_2\{4\text{-}S(CH_3)N_2OC_4H_2\}][PF_6]$ ($M = Mo$ and W)

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Abstract—Cationic complexes $[MoCp_2(U)][PF_6]$ (**1**), $[MCp_2(2TU)][PF_6]$ (**2, 2′**), $[MCp_2(4TU)][PF_6]$ (**3, 3′**), $[MoCp_2(2,4\text{-}DTU)]Cl$ (**4**), $[MCp_2(2MTU)][PF_6]$ (**5, 5′**) and $[MCp_2(4MTU)][PF_6]$ (**6, 6′**) ($M = Mo, W$; $Cp = \eta^5\text{-}C_5H_5$; U = uracilato; 2TU = 2-thiouracilato; 4TU = 4-thiouracilato; 2,4-DTU = 2,4-dithiouracilato; 2MTU = 2-methylthiouracilato and 4MTU = 4-methylthiouracilato) have been prepared from the reaction of $[MCp_2Cl_2]$ with the corresponding uracil in the presence of triethylamine. All the uracilato derivatives act as bidentate ligands and experimental evidence (X-ray and IR) shows the following preference for binding atoms in this system: $N(3) > N(1)$, $=S > =O$, $O(2) > O(4)$; although there is no clear evidence it is also likely that $S(2) > S(4)$. Electrochemical studies, by cyclic voltammetry carried out in acetonitrile or dimethylformamide, showed that compounds where ligands coordinate through N,S atoms are more stable upon oxidation than compounds where ligands coordinate through N,O donor atoms. The molecular structures of $[MoCp_2(2TU)][PF_6]$(**2**), $[WCp_2(2TU)][PF_6]$(**2′**), $[MoCp_2(4TU)][PF_6]$(**3**), $[MoCp_2(2MTU)][PF_6]$(**5**), $[WCp_2(2MTU)][PF_6]$(**5′**) and $[MoCp_2(4MTU)][PF_6]$(**6**) have been determined by X-ray crystallography.

In recent years there has been some interest in metal complexes with uracil and its derivatives. The interest stems not only from the existence of different possible ways of coordination of the ligands to the metal centre but also from the potential biological importance of the metal–ligand interaction.[1,2] Following our interest in the chemistry of MCp_2 complexes with N, O or S donor ligands[3] and MCp_2X_2 complexes being highly active agents against a variety of tumour cell lines,[4] we decided to synthesize and characterize $MoCp_2$ complexes with uracil (HU), 2-thiouracil (2HTU), 4-thiouracil (4HTU),

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2,4-dithiouracil (2,4HDTU), 2-methylthiouracil (2HMTU) and 4-methylthiouracil (4HMTU) and WCp_2 complexes with 2HTU, 4HTU, 2HMTU and 4HMTU. These complexes were fully characterized and their electrochemistry was studied by cyclic voltammetry. Molecular structures were determined for $[MCp_2(2TU)][PF_6]$, $[MoCp_2(4TU)][PF_6]$, $[MCp_2(2MTU)][PF_6]$ and $[MoCp_2(4MTU)][PF_6]$, with M = Mo and W.

EXPERIMENTAL

Synthesis of the complexes

All the organometallic preparations and further manipulations were carried out under nitrogen using Schlenk-tube techniques.

IR spectra were measured on a Perkin–Elmer 683 spectrophotometer with KBr pellets. ^1H NMR spectra were recorded on a VARIAN Unity 300 spectrometer. Microanalyses were performed in our laboratories.

The compounds $[MCp_2Cl_2]$ were prepared from the parent dihydrides $[MCp_2H_2]$.[5]

Ligands HU and 2HTU were obtained from Aldrich Chemical Company (Milwaukee, Wisconsin, U.S.A.) and used as received. Purity was checked by ^1H NMR and IR spectroscopy and by elemental analysis.

Ligands 4HTU and 2,4HDTU were synthesized by reaction with P_2S_5 in H_2O/dioxane, using an adaptation of methods described in the literature.[6]

2HMTU and 4HMTU were synthesized by quantitative methylation of 2HTU and 4HTU, respectively, with methyl iodide.[6]

Preparation of $[MCp_2(Ur)][PF_6]$ (M = Mo *and* W) (Ur = U, 2TU, 4TU, 2MTU and 4MTU). MCp_2Cl_2 ($\approx$3.3 mmol) was refluxed with the appropriate ligand (1 : 1) in ethanol in the presence of excess triethylamine. The reaction mixture was filtered and the filtrate was pumped to dryness *in vacuo*. The residue was extracted with water and NH_4PF_6 was added. Crystals were obtained either by slow evaporation of this solution or by filtering it and recrystallizing the residue from acetone.

Preparation of $[MoCp_2(2,4\text{-}DTU)]Cl$. $MoCp_2Cl_2$ ($\approx$2.2 mmol) was refluxed with 2,4HDTU (1 : 1) in ethanol in the presence of excess triethylamine. After 24 h, a salmon coloured precipitate separates. The reaction mixture was filtered and the precipitate was washed with water, acetone and ethyl ether and dried *in vacuo*.

All the formulations proposed were supported by analytical data (Table 1) and also by IR and ^1H NMR spectra (Table 2). The insolubility of **4** in most of the common solvents prevented its further purification which may account for the poor analytical results. Although compound **6** has been fully characterized by X-ray structure we were unable to obtain a better carbon analysis.

X-Ray structural determination

Details for data collection and structure determination are included in Table 3.

For compound **2** the Mo atom was located from a Patterson map and was found to be at a special position (*m*). All the other non-hydrogen atoms were located from subsequent difference Fourier syntheses. The 2TU ligand was also found to lie in the symmetry plane *m*. The hydrogen atoms of the 2TU ligand were located and refined. The Cp hydrogens were included in idealized positions, riding in the parent carbon atom with refined isotropic temperature factors.

For compound **2′** the coordinates of compound **2** were used as starting values and refined by least-squares methods.

In compound **3** the heavy Mo atom was located from a Patterson map, and the other non-hydrogen atoms were found from subsequent difference Fourier syntheses. The hydrogen atoms of the 4TU ligand were located and refined while those in the Cp rings were inserted in idealized positions, riding in the parent carbon atom, with no constraints in the isotropic temperature factors. The PF_6 anion was refined using a disorder model where each of the six F atoms was positioned in three possible sites.

For compound **5** the Mo atom was located from a Patterson map and all the other non-hydrogen atoms were located from subsequent difference Fourier syntheses. The carbon atoms of the Cp rings were refined with isotropic temperature factors. The hydrogen atoms of the 2MTU ligand were located and refined. The Cp and methyl hydrogens were included in idealized positions, riding in the parent carbon atom with fixed isotropic temperature factors.

For compound **5′** the structure was solved by using the heavy atom technique and all the non-metal atoms were found in subsequent difference Fourier maps.

For compound **6** the two independent Mo atoms were located from a Patterson map and all the other non-hydrogen atoms from subsequent difference Fourier syntheses. The hydrogen atoms of the 4MTU ligand were located and refined. The Cp hydrogens were included in idealized positions, riding in the parent carbon atom, and a common isotropic temperature factor for the hydrogens of each Cp ring was also refined.

Table 1. Analytical data

Compound	Colour	Analysis (%) ; found (req.) C	H	N
$[MoCp_2(U)][PF_6]$	Greyish green	34.9(34.9)	2.9(2.7)	5.8(5.8)
$[MoCp_2(2TU)][PF_6]$	Coral	32.6(33.7)	2.7(2.6)	5.6(5.6)
$[WCp_2(2TU)][PF_6]$	Brick	28.9(28.7)	2.6(2.2)	4.9(4.8)
$[MoCp_2(4TU)][PF_6]$	Dark red	34.7(33.8)	2.9(2.6)	5.6(5.6)
$[WCp_2(4TU)][PF_6]$	Brick	28.2(28.7)	2.7(2.2)	4.9(4.8)
$[MoCp_2(2,4TU)][PF_6]$	Salmon	44.3(41.5)	3.5(3.2)	7.3(6.9)
$[MoCp_2(2MTU)][PF_6]$	Brick	35.0(35.2)	3.0(3.0)	5.6(5.5)
$[WCp_2(2MTU)][PF_6]$	Dark brown	28.1(30.0)	2.7(2.5)	4.7(4.1)
$[MoCp_2(4MTU)][PF_6]$	Brown	28.8(35.2)	3.3(3.0)	5.8(5.5)
$[WCp_2(4MTU)][PF_6]$	Dark red	28.6(30.0)	2.6(2.5)	5.1(4.1)

Supplementary material on all the complexes has been deposited at the Cambridge Crystallographic Database, and comprises atom coordinates, atomic thermal motion parameters, remaining bond lengths and angles and tables of observed and calculated structure factors.

Structure solution and refinement were done with SHELX76[7] and all the molecular drawings were drawn with ORTEP-II.[8] The atomic scattering factors and anomalous scattering terms were taken from international tables.[9]

Electrochemical procedure

The electrochemical instrumentation consisted of a Princeton Applied Research Model 173 potentiometer, a model 175 voltage programmer, a model 179 digital coulometer and an Omnigraphic 2000 X-T recorder from Houston Instruments. Potentials were referred to a calomel electrode containing a saturated solution of potassium chloride which was checked relative to a 1.0×10^{-3} M solution of ferrocene in acetonitrile containing 0.10 M $LiClO_4$ for which the ferricinium/ferrocene potential was in agreement with the literature.[10] The working electrode was made of a 2 mm piece of platinum wire for cyclic voltammograms, while the working electrode in the controlled potential electrolysis experiments was a platinum gauze. The secondary electrode was a platinum wire coil. Cyclic voltammetry experiments were performed in a PAR polarographic cell at room temperature, the solutions being used were 1 mM in solute and 0.1 M in supporting electrolyte, tetrabutylammonium hexafluorophosphate.

The solvents, CH_3CN and CH_2Cl_2, which were reagent grade materials, were dried over CaH_2 and P_2O_5 and were distilled just before use under argon. Solutions were degassed with dry nitrogen before each experiment and a nitrogen atmosphere was maintained over the solution during the experiments.

RESULTS AND DISCUSSION

Chemical studies

In order to obtain uracils as anionic ligands, a standard synthetic route to dicyclopentadienylmolybdenum derivatives was followed by direct reaction of MCp_2Cl_2 with the required uracil in the presence of a strong deprotonating agent. All the ligands coordinate in a bidentate fashion and the cationic complexes were isolated as the hexafluorophosphate salts, except for complex **4** where the chloride salt was insoluble in water so that the PF_6 salt could not be prepared.

Typical IR bands confirm the presence of the MCp_2 fragment (≈ 3100 cm^{-1}) and of the PF_6^- anion (840 and 560 cm^{-1}) in all complexes. Characteristic bands of the uracil ligands were also assigned based on the comparison with the spectra of the free ligands and on data reported in the literature.

In the case of the uracilate complex $[MoCp_2(U)][PF_6]$ we observe that bands at 1417 cm^{-1}, assigned to $\delta N(3)—H$ and at 1718 cm^{-1}, assigned to $\nu[C(2)=O]$ in the free ligand, were not observed in the IR spectrum of the complex while new bands appeared at 1575 cm^{-1}, assigned to $\nu[C—O]$[11] which suggests coordination of this ligand to the metal through N(3) and O(2) donor atoms although we have not been able to prepare crystals suitable for X-ray analysis.

Table 2. ^1H NMR and IR data

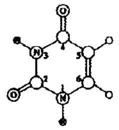
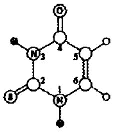
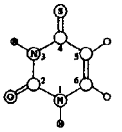
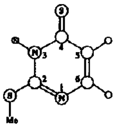
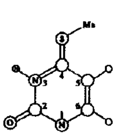
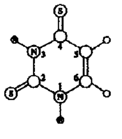
Compound	CH_3	H_5	H_6	η^5-C_5H_5	N—H	IR main bands
[MoCp$_2$(U)][PF$_6$]		5.35; 5.33 (d,1)	7.80 (d,1)	6.09 (s,10)	11.5 (s,1)	3120m, 1640m, 1620m, 1575s, 1455m, 1360m, 1290s, 1190vs, 860s, 820m, 550s
		5.43 (d,1)	7.38 (d,1)		10.9 (s,2)	
[MoCp$_2$(2TU)][PF$_6$]		5.841; 5.866 (d,1)	7.581; 7.606 (d,1)	5.769 (s,10)	Not detected	3120m, 3000m, 1640m, 1630m, 1620s, 1610s, 1530s, 1440s, 1410m, 1270s, 1200s, 1020m, 1000m, 840vs, 820s, 575m, 550vs, 430w, 400w
[WCp$_2$(2TU)][PF$_6$]		5.85; 5.87 (d,1)	7.53; 7.56 (d,1)	5.59 (s,10)	7.15	3120m, 3010m, 1640m, 1630m, 1620s, 1610s, 1530m, 1440s, 1400s, 1270s, 1200s, 1020m, 1000m, 830vs, 580m, 560vs, 430w, 370w
		5.791; 5.816 (d,1)	7.385; 7.411 (d,1)		12.37 (s,2)	
[MoCp$_2$(4TU)][PF$_6$]		5.946; 5.969 (d,1)	7.778; 7.800 (d,1)	5.795 (s,10)	11.9 (s,1)	3120m, 2920w, 1675vs, 1590s, 1445s, 1390m, 1240m, 1150s, 1025m, 830vs, 625m, 600w, 550vs, 425w
[WCp$_2$(4TU)][PF$_6$]		6.21; 6.22 (d,1)	8.32; 8.35 (d,1)	6.18 (s,10)	12.51(s,1)	3120m, 2920w, 1675s, 1580s, 1450s, 1390m, 1240m, 1150m, 1025m, 830vs, 620m, 600w, 545vs, 425w
		6.150; 6.171 (d,1)	7.319; 7.341 (d,1)		11.5–12.5 (s,2)	
[MoCp$_2$(2MTU)][PF$_6$]	2.495 (s,3)	5.864; 5.889 (d,1)	7.604; 7.629 (d,1)	5.791 (s,10)		3120m, 2920w, 1655s, 1575w, 1525w, 1440m, 1340m,1265s, 1200m, 1070m, 1115m, 830vs, 620m, 540vs
[WCp$_2$(2MTU)][PF$_6$]	2.546 (s,3)	5.929; 5.950 (d,1)	8.392; 8.413 (d,1)	6.140 (s,10)		3120m, 2920w, 1570s, 1540m, 1440m, 1425s, 1350s, 1240m, 1020m, 830vs, 620m, 540vs
	2.443 (s,3)	6.052; 6.073 (d,1)	7.825; 7.846 (d,1)		Broad (s,1)	
[MoCp$_2$(4MTU)][PF$_6$]	2.399 (s,3)	6.846; 6.887 (d,1)	7.664; 7.680 (d,1)	6.018 (s,10)		3120m, 2950w, 1585vs, 1520m, 1465m, 1400s, 1310s, 1150m, 1125m, 975m, 950m, 830vs, 740m, 630w, 550vs, 450w
[WCp$_2$(4MTU)][PF$_6$]	2.40 (s,3)	6.92; 6.94 (d,1)	7.88; 7.92 (d,1)	6.0 (s,10)		3120m, 3010w, 1575vs, 1520m, 1460s, 1400s, 1305s, 1150s, 1130m, 975m, 950m, 830vs, 740m, 635w, 546vs, 450w, 375w
	2.398 (s,3)	6.257; 6.289 (d,1)	7.573; 7.595 (d,1)		11.442 (s,1)	
[MoCp$_2$(2,4DTU)]Cl		6.62; 6.64 (d,1)	7.28; 7.32 (d,1)	5.631 (s,10)	Not detected	3100m, 1545s, 1455s, 1390s, 1280s, 1200m, 1150s, 835s, 805m, 705m
		6.47; 6.501 (d,1)	7.240; 7.263 (d,1)		13.3 (s,1)	

Table 3. Crystal data

Formula	$[MoCp_2(2TU)][PF_6]$	$[WCp_2(2TU)][PF_6]$	$[MoCp_2(4TU)][PF_6]$	$[MoCp_2(2MTU)][PF_6]$	$[WCp_2(2MTU)][PF_6]$	$[MoCp_2(4MTU)][PF_6]$
Diffractometer	Enraf–Nonius TURBO-CAD4	Philips PW 1100	Enraf–Nonius CAD4	Enraf–Nonius TURBO-CAD4	Philips PW 1100	Enraf–Nonius CAD4
Scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Diffractometer range	1.5–30°	2.5–60°	1.5–25°	1.5–25°	2.5–60°	1.5–25°
No. of unique reflections	2975	1423	4537	1482	1504	4680
No. of reflections used in refinement having $F > n\sigma(F)$	1499	642	3855	1346	1239	3357
n	3	3 $[I > 3\sigma(I)]$	3	1.5	3 $[I > 3\sigma(I)]$	3
Final R	0.048	0.041	0.054	0.071	0.044	0.041
Final R_w	0.051	0.044	0.062	0.049	0.045	0.050
Weighting scheme w	$1.272/[\sigma(F^2)+0.000978\ F^2]$	$1/\sigma(I)$	$2.556/[\sigma(F^2)+0.000378\ F^2]$	$0.875/[\sigma(F^2)+0.0001\ F^2]$	$1/\sigma(I)$	$0.857/[\sigma(F^2)+0.001\ F^2]$
Formula weight	498.23	585.14	498.23	512.25	599.17	512.25
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pnm2_1$	$Pnm2_1$	$P2_1/c$	$P2_1$	$P2_1/m$	$P2_1$
a (Å)	6.8471(5)	6.862(1)	7.8824(6)	9.338(2)	9.300(1)	10.358(2)
b (Å)	9.2984(5)	9.230(1)	14.723(1)	8.701(7)	8.688(2)	12.947(3)
c (Å)	13.0519(7)	13.093(3)	15.087(1)	11.063(3)	11.068(3)	14.165(4)
β (°)			98.338(6)	96.65(2)	96.58(1)	106.09(2)
V (Å^3)	831.0	829.26	1732.3	892.8	888.39	1825.1
Z	2	2	4	2	2	4
D_c	1.99	2.34	1.51	1.51	2.29	1.88
μ	9.65	158.6	9.26	8.98	148.43	8.80
Radiation	Mo-K_α(0.71069)	Cu-K_α(1.5418)	Mo-K_α(0.71069)	Mo-K_α(0.71069)	Cu-K_α (1.5418)	Mo-K_α(0.71069)

X-Ray structural analysis

X-Ray analysis showed discrete cation and anion molecules in the crystals of the six complexes, but in **6** there are two cations and two anions per asymmetric unit. Molecular diagrams of the cations with the atomic numbering scheme are shown in Figs 1–6. Selected bond lengths and angles are presented in Table 4.

The cations adopt the usual bent metallocene geometry, with Cp—M—Cp angles of 136.2 (**2**), 133.2 (**2′**), 134.6 (**3**), 134.4 (**5**), 133.2 (**5′**) and 133.1/131.5° (**6**) respectively, with average M—Cp distances of 1.981, 1.950, 1.964, 1.964, 1.966 and 1.958/1.965 Å. The L ligand is practically in the plane bisecting the Cp—M—Cp angle, and in 2TU (**2**, **2′**) and 2MTU (**5′**) complexes both the M atom and the uracil ligands lie in a crystallographic mirror plane. The remaining coordination positions of the pseudo tetrahedral coordination geometry are occupied by the N and S atoms of the 2TU and 4TU ligands, and in the methylated derivatives by the equivalent N and O atoms of the ligand. The Mo—N distances ranging from 2.137(7) in 4MTU to 2.169(10) Å in 2MTU agree with the values found in similar compounds, like 2.160(8) in $MoCp_2(2\text{-}NHNC_5H_4)$,[12] 2.157(5) in $MoCp_2(2\text{-}SNC_5H_4)$[3] and 2.138(11) in $MoCp_2(2\text{-}ONC_5H_4)$,[12] being slightly shorter than 2.173(3) in $MoCp_2$(9-methyladenyl)[2] and longer than 2.130(5) in $MoCp_2$(1-methylcytosyl).[2] The Mo—O distances, respectively 2.167(10) in 2MTU and 2.131(7)/2.139(7) in 4MTU agree well with the values found in $MoCp_2XY$ (Y can be X) complexes with O donor atoms [ranging from 2.050 to 2.142 Å] (refs 10 and 13, and refs therein). However, one would say that the 2.167(10) distance is clearly longer than the values usually found. Also the Mo—S bonding distance [2.479(4) in 2TU and 2.516(4) in 4TU] is within the expected values for this family of compounds [2.500(4) in $MoCp_2(2\text{-}SNC_5H_4)$].[3]

The N—Mo—S, O angle is, as expected, smaller than the X—Mo—Y angle in $MoCp_2XY$ complexes, "showing" the strain imposed by the small bite of the ligand. The values obtained 65.3(3) (2TU), 61.4(4) (2MTU), 64.3(2) (4TU) and 60.1(3)/60.9(3) (4MTU) are comparable to 60.9(1) in $MoCp_2$(9-methyladenyl),[2] 59.9(1) in $MoCp_2$(1-methylcytosyl),[2] 59.8(3) in $MoCp_2(2\text{-}NHNC_5H_4)$,[12] 61.2(4) in $MoCp_2(2\text{-}ONC_5H_4)$,[12] 64.9(2) in $MoCp_2(2\text{-}SNC_5H_4)$[3] and 66.1(2)° in $MoCp_2(SO_4)$.[12] These results once again agree with the theoretical value (63°) predicted by extended Hückel calculations in the model cation $[MoCp_2(2\text{-}NHNC_5H_4)]^+$,[12] showing that the shorter angles

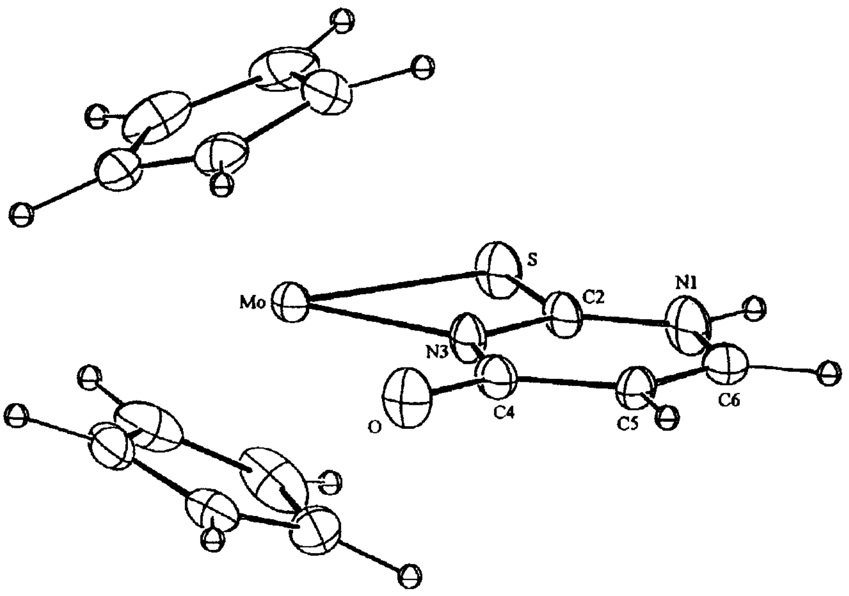


Fig. 1. Molecular structure of $[MoCp_2(2\text{-}SN_2OC_4H_3)][PF_6]$.

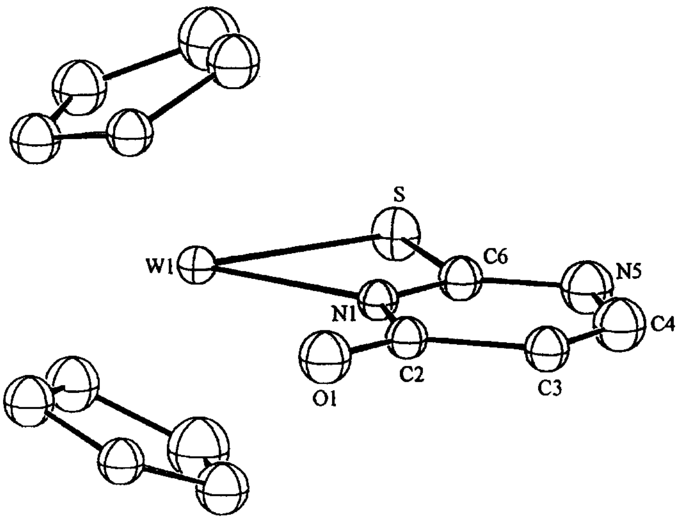


Fig. 2. Molecular structure of $[WCp_2(2\text{-}SN_2OC_4H_3)][PF_6]$.

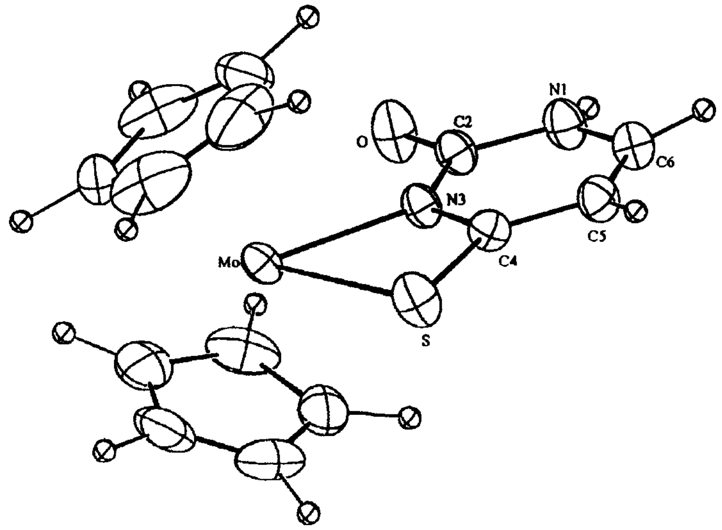


Fig. 3. Molecular structure of $[MoCp_2(4\text{-}SN_2OC_4H_3)][PF_6]$.

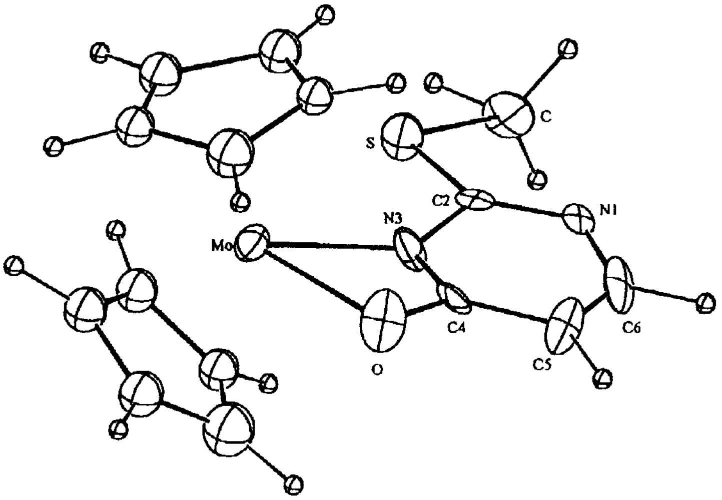


Fig. 4. Molecular structure of $[MoCp_2(2\text{-}S(Me)N_2OC_4H_2)][PF_6]$.

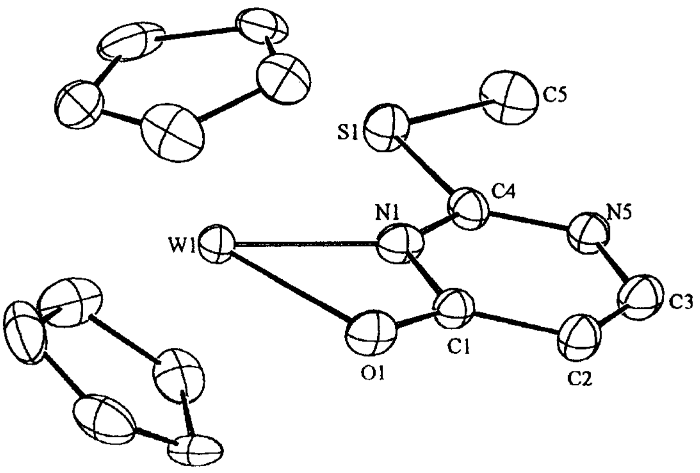


Fig. 5. Molecular structure of $[WCp_2(2\text{-}S(Me)N_2OC_4H_2)][PF_6]$.

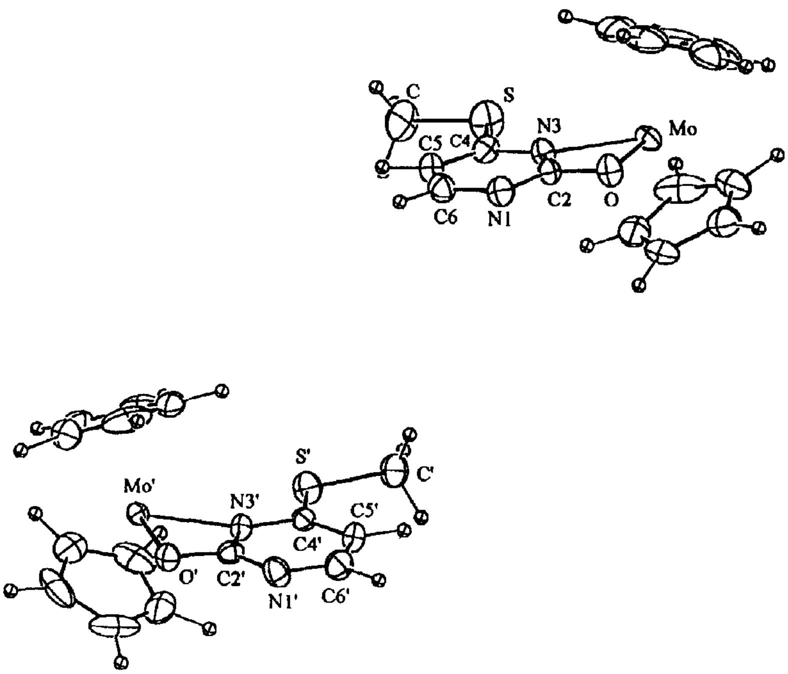


Fig. 6. Molecular structure of [MoCp$_2$(4-S(Me)N$_2$OC$_4$H$_2$)][PF$_6$].

Table 4. Selected bond lengths (Å) and angles (°)

	[MoCp$_2$(2TU)] [PF$_6$]	[WCp$_2$(2TU)] [PF$_6$]	[MoCp$_2$(4TU)] [PF$_6$]	[MoCp$_2$(2MTU)] [PF$_6$]	[WCp$_2$(2MTU)] [PF$_6$]	[MoCp$_2$(4MTU)] [PF$_6$]
M—Cp (av)	1.981	1.950	1.964	1.964	1.966	1.961
M—N	2.152(11)	2.255(20)	2.139(5)	2.175(10)	2.161(14)	2.166(7)/2.137(7)
M—S	2.479(4)	2.495(7)	2.516(4)	—	—	—
M—O	—	—	—	2.163(9)	2.168(10)	2.131(7)/2.139(7)
C—S	1.700(14)	1.763(28)	1.712(6)	1.738(14)	1.741(16)	1.735(10)/1.732(9)
C—O	1.227(10)	1.180(35)	1.212(5)	1.294(13)	1.295(20)	1.274(9)/1.290(9)
S—Me	—	—	—	1.738(14)	1.808(22)	1.780(10)/1.804(9)
N1—C2	1.311(17)	1.246(34)	1.373(6)	1.301(13)	1.321(21)	1.320(9)/1.326(10)
C2—N3	1.335(12)	1.352(42)	1.376(6)	1.359(16)	1.311(19)	1.338(9)/1.352(10)
N3—C4	1.400(16)	1.423(52)	1.342(5)	1.362(15)	1.353(21)	1.311(9)/1.351(9)
C4—C5	1.454(17)	1.246(63)	1.391(6)	1.408(14)	1.374(26)	1.406(11)/1.358(10)
C5—C6	1.313(21)	1.513(42)	1.346(7)	1.350(18)	1.374(22)	1.358(11)/1.406(12)
N1—C6	1.388(21)	1.432(34)	1.339(6)	1.365(17)	1.374(19)	1.333(10)/1.348(10)
Cp—M—Cp	136.2	133.2	134.6	134.4	133.2	132.3
N—M—O	—	—	—	61.3(4)	60.9(4)	60.1(3)/60.9(3)
N—M—S	65.3(3)	64.0(5)	64.3(2)	—	—	—
M—S—C	80.8(4)	80.5(9)	81.0(2)	—	—	—
M—O—C	—	—	—	94.1(7)	95.3(9)	96.3(5)/95.2(5)
M—N—C(S)	102.8(8)	102.7(17)	105.6(3)	144.2(12)	146.6(11)	145.6(5)/146.5(5)
M—N—C(O)	135.2(6)	133.6(16)	131.5(2)	91.6(8)	93.2(9)	92.7(5)/93.5(5)
N(M)—C—O	120.8(11)	121.2(26)	122.5(4)	112.8(10)	110.6(13)	110.9(7)/110.3(7)
N(M)—C—S	111.2(9)	112.9(20)	109.0(4)	112.2(10)	114.3(11)	115.3(6)/113.5(6)
C—N(M)—C	122.0(10)	123.7(22)	122.9(4)	119.8(12)	120.2(13)	121.7(7)/120.0(7)
C—S—Me	—	—	—	99.9(7)	101.0(9)	102.0(5)/102.1(5)

result from the balance between making strong metal–ligand bonds without deforming the strained ligand too much.[12] There seems to be no correlation between the Cp—Mo—Cp and the L—Mo—L angle as explained before.[12]

The angles within the metallocycle are restricted by the chelation to the metal atom, the N—M—S angles being larger than N—M—O due to larger S—C bond lengths (Fig. 7).

The presence of a hydrogen bond to the exocyclic nitrogen atom in the 2TU and 4TU derivatives allows a perfect geometry for intermolecular hydrogen bonds. In the 2TU derivative the oxygen atom and the exocyclic nitrogen are in a *para* position relative to each other, making possible the existence of an infinite chain of hydrogen bonds between *a* translated molecules (Fig. 8). However, in the 4TU derivative, those atoms are *ortho* positioned creating dimers of hydrogen bonded molecules (Fig. 9).

Electrochemical studies

The electrochemical behaviour of molybdenum and tungsten compounds was investigated by cyclic voltammetry in acetonitrile (Table 5) and dimethylformamide, in the limits of the solvent, with tetrabutylammonium as a supporting electrolyte.

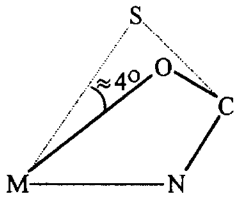


Fig. 7. Influence of the S, O—C bond length in the N—M—S, O angle.

Molybdenum compounds presented one redox wave, attributed to the $Mo^{IV} \rightarrow Mo^{V}$ pair in the range ≈1.140–1.240 V, its reversibility depended on whether the chelating ligand was 2- or 4-thiouracil or the corresponding methylthiouracils. These situations are illustrated in Fig. 10.

The identification of this redox wave was based on our previous electrochemical studies on related compounds.[3] For the reversible waves, the average of the anodic and cathodic peak potentials was independent of the scan speed and the separation of the waves ΔE_p was *ca* 70 mV (Table 5). A plot of i_a against the square root of the scan speed (20, 50, 100, 200 and 500 mV s^{-1}) was linear over the range of those potentials, as expected for a diffusion-controlled electrode process.

The electrochemical studies for tungsten compounds showed a quite similar behaviour when compared with the molybdenum analogues, although the process $W^{IV} \rightarrow W^{V}$ may occur at lower potentials (range 0.90–1.10). The easier oxidation of tungsten compounds relatively to the molybdenum analogues has been found before for other related compounds.[3]

The reversibility of compound $[WCp_2(4TU)][PF_6]$ was proved by the usual tests, based on different speed scanning electrochemical data, mentioned above.

Interestingly, it seems that 4-thiouracil gives, in the case of the tungsten compound, more stability to the oxidation of the organometallic moiety than

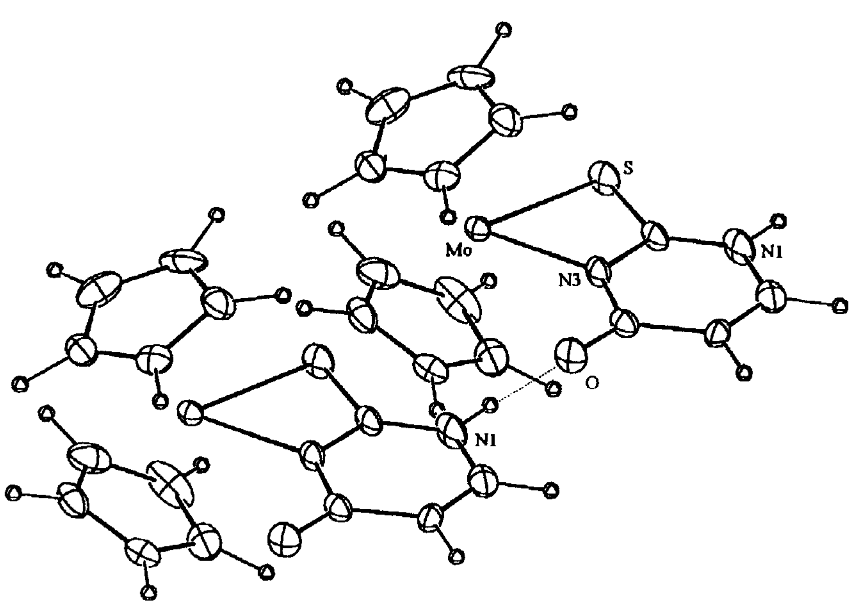


Fig. 8. The hydrogen bonding system in $[MoCp_2(2\text{-}SN_2OC_4H_3)]^+$ metal centre.

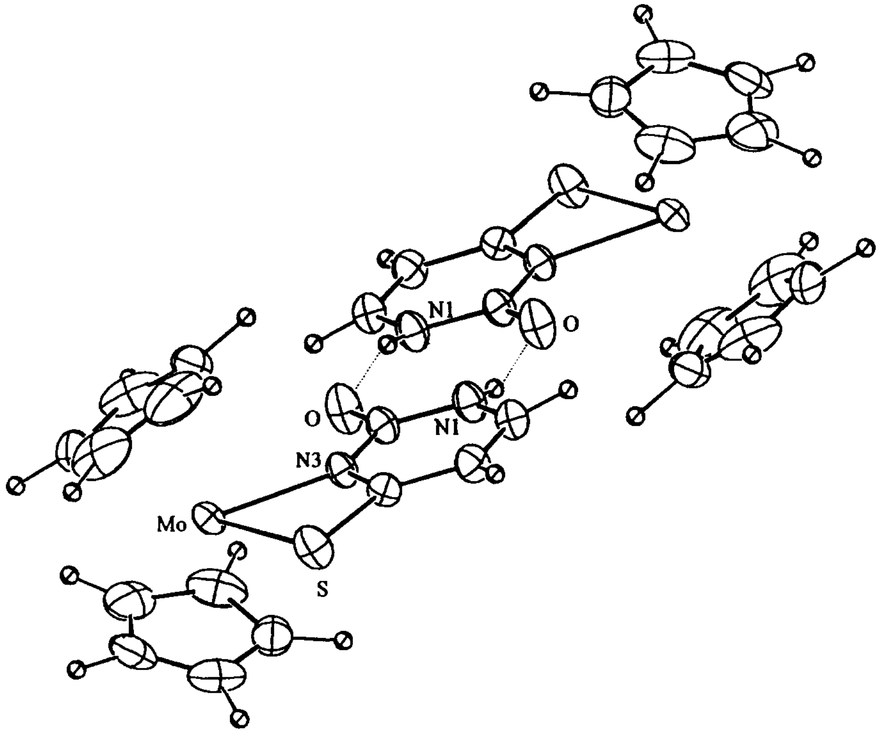


Fig. 9. The hydrogen bonding system in $[MoCp_2(4\text{-}SN_2OC_4H_3)]^+$ metal centre.

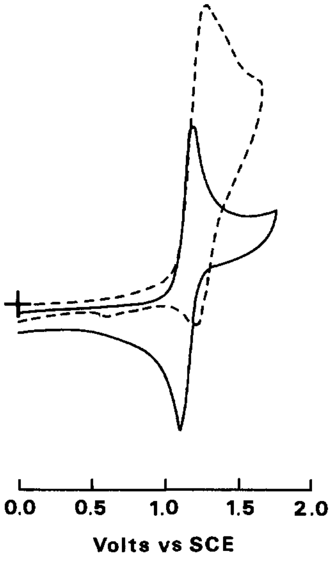


Fig. 10. Cyclic voltammogram of $[MoCp_2(4\text{-}SN_2OC_4H_3)][PF_6]$ and $[MoCp_2(4\text{-}S(Me)N_2OC_4H_2)][PF_6]$ (dashed line) in acetonitrile.

2-thiouracil, in spite of the fact that the W, N, S four membered ring remained the same in both cases, as shown by X-ray structural data.

Given the insolubility in acetonitrile of some of the compounds, studies were carried out also in dimethylformamide. In this solvent, the oxidation waves were totally irreversible even for the compounds which behaved reversibly in acetonitrile, and only a very intensive anodic wave was found without any corresponding cathodic counterpart.

Our previous studies on other bis-η^5-cyclopentadienylmolybdenum/tungsten complexes with chelated substituted pyridines, namely $[MoCp_2(2\text{-}SNC_5H_4)]^+$, $[MoCp_2(2\text{-}ONC_5H_4)]^+$ and $[MoCp_2(2\text{-}NHNC_5H_4)]^{+3}$ showed a quasi-reversible behaviour in the case where sulphur was the second coordinated atom on the substituted pyridine ligand and irreversibility in the other two compounds. This observation was in good agreement with X-ray structural data which showed a less strained structure in the heterometallic ring for the sulphur case.[3]

The results presented in this work, showing reversible electrochemical oxidations for compounds having sulphur as the second coordinated atom (2- and 4-thiouracils) instead of oxygen (2- and 4-methylthiouracils), are in good agreement with the well-known stability role of the sulphur on molybdenum systems.

Table 5. Electrochemical data[a]

Compound	E_{pa}(V)	E_{pc}(V)	$E_p/2$(V)	ΔE (mV)	i_a/i_c
$[MoCp_2(2TU)][PF_6]$	1.220	1.130	1.175	70	≅1 (rev.)
$[MoCp_2(4TU)][PF_6]$	1.175	1.110	1.138	75	≅1 (rev.)
$[MoCp_2(2MTU)][PF_6]$	1.225	1.075	1.150	150	Irrev.
$[MoCp_2(4MTU)][PF_6]$	1.275	1.200	1.237	75	Irrev.
$[WCp_2(2TU)][PF_6]$	1.070	0.970	1.020	100	0.9
$[WCp_2(4TU)][PF_6]$	1.050	0.960	1.005	90	≅1 (rev.)
$[WCp_2(4MTU)][PF_6]$	0.887	—	—	—	—

[a] All electrochemical measurements performed in CH_3CN containing 0.1 M Bu_4NPF_6. Potentials are referenced to a calomel electrode containing a saturated KCl solution. Sweep rates of 200 mV s^{-1} were commonly used and the temperature was 20 ± 2°C.

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