# COMPLEXES OF ESCULETIN WITH SECOND AND THIRD ROW TRANSITION ELEMENTS

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Abstract—The new esculetin (H<sub>2</sub>esc; 6,7-dihydroxy coumarin) complexes *cis*-[MO<sub>2</sub>(esc)<sub>2</sub>]<sup>2-</sup>,  $[M_2O_5(esc)_2]^{2-}$  (M = Mo, W), *trans*-[UO<sub>2</sub>(esc) · MeOH], *trans*-[OsO<sub>2</sub>(esc)<sub>2</sub>]<sup>2-</sup>, [M(esc)<sub>3</sub>]<sup>2-</sup> (M = Os, Re, Ir),  $[M(esc)_3]^{3-}$  (M = Fe, Rh),  $[Ru(bipy)(esc)_2]$ , [ML(esc)] [M = Pd, Pt; L = (PPh<sub>3</sub>)<sub>2</sub>, bipy] and [ReOI(PPh<sub>3</sub>)<sub>2</sub>(esc)] have been prepared. Their Raman, IR, <sup>1</sup>H and <sup>13</sup>C NMR and mass spectra have been measured, and cyclic voltammograms of some of them recorded.

Esculetin (H<sub>2</sub>esc; 6,7-dihydroxy coumarin; 6,7dihydroxy-2H-1-benzopyran-2-one; see Fig. 1) is of interest since it contains the non-innocent catechol grouping, and is biologically important as a lipoxygenase inhibitor.<sup>1</sup> We have reported catechol complexes of a number of second and third row elements including molybdenum,<sup>2</sup> tungsten,<sup>2</sup> rhenium,<sup>2,3</sup> ruthenium,<sup>2</sup> osmium,<sup>2,4-6</sup> palladium and platinum,<sup>7,8</sup> and complexes with related ligands such as pyrogallol,<sup>7</sup> naphthalene-2,3-diol<sup>8</sup> and catecholamines.<sup>9</sup> In this paper we explore the coordination chemistry of esculetin with a number of second and third row elements and discuss the structures of the products on the basis of their vibrational, NMR and mass spectra.

Few complexes of esculetin with transition metals have been reported; the only ones which have been isolated are  $[Cp_2Ti(esc)]$ ,<sup>10</sup>  $[Cu(esc)L_4]$  (L = NH<sub>3</sub>, py)<sup>11</sup> and  $[Cu(escH)_2(H_2O)_2]$ .<sup>12</sup>

# **RESULTS AND DISCUSSION**

# (1) Preparation of the complexes

The esculetin oxo-complexes  $[MO_2(esc)_2]^{2-}$ (M = Mo, W, Os),  $[M_2O_5(esc)_2]^{2-}$  (M = Mo, W) and UO<sub>2</sub>(esc) · MeOH were prepared using methods similar to their catecholato analogues<sup>2,4</sup> from  $[MO_4]^{2-}$  (M = Mo, W), *trans*- $[OsO_2(OH)_4]^{2-}$ or uranyl acetate with the ligand and the appro-

priate cation in ethanol. The tris species  $[M(esc)_3]^{2-1}$ (M = Re, Ir, Os) were obtained from  $[MCl_6]^{2-1}$ and esculetin in the presence of aqueous KOH, and similar methods were used for  $[M(esc)_3]^{3-1}$ (M = Rh, Fe) starting with MCl<sub>3</sub>·nH<sub>2</sub>O. The  $M(PPh_3)_2(esc)$  and M(bipy)(esc) complexes (M = Pd, Pt) were made from  $[M(PPh_3)_2Cl_2]$  and [M(bipy)Cl<sub>2</sub>], respectively, with the ligand in alcohol in the presence of aqueous base. The complex [ReOI(PPh<sub>3</sub>)<sub>2</sub>(esc)] was made from [ReO<sub>2</sub>I(PPh<sub>3</sub>)<sub>2</sub>] and the ligand in ethanol, while [Ru(bipy)(esc)<sub>2</sub>] was made in an analogous fashion to [Ru(bipy)(cat)<sub>2</sub>]<sup>13</sup> from [Ru(bipy)Cl<sub>3</sub> and esculetin in methanol in the presence of NaOH. We were unable to obtain crystals suitable for X-ray crystal structure determinations.

### (2) Vibrational spectra

The Raman and IR spectra of esculetin and its complexes are reported in Table 1. The general features are similar to those observed for catechol and their complexes.<sup>3,9</sup> In the IR spectra the stretching vibration v(OH) in the range 3200–



Fig. 1. Esculetin, with the atoms numbered.

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										IN H <sub>1</sub>	ИR	
		Ana	lysis			Vibrati	ional spectra		$H_3$	H4	H,	H
Complex	C	Н	Z	Ňa	v(C-C)	v(CO)	$v_{\rm s}(\rm MO_2)$	$v_{as}(MO_2)$	(p)	(p)	(s)	(s)
H,esc					1466s	1281			6.15	7.85	6.96	6.73
4					1400s	1270s						
Na <sub>3</sub> [MoO <sub>2</sub> (esc) <sub>2</sub> ] • 2H <sub>2</sub> O	38.5	2.4		8.2	1486s	1262s	914s	883s	6.16	7.83	6.85	6.55
	(38.5)	(2.2)		(8.2)	14905	1264s	908s	886m				
$(PPh_4)_2[MoO_3(esc)_3] \cdot 4H_3O$	64.1	4.6			1489s	1257s	924s	903s	5.80	7.53	6.30	6.08
	(64.4)	(4.6)			1490s	1260m	940m	906m				
$(Et_4N)_2[Mo_2O_5(esc)_2] \cdot 4H_2O$	42.6	6.1	3.0		1490s	1269s	922s	904s	5.83	7.55	6.30	6.11
	(42.7)	(5.9)	(2.9)		1490s	1262m	927m	900w				
$(PPh_4)_2[WO_2(esc)_2] \cdot 5H_2O$	59.2	3.9			1484s	1257s	919s	875s	5.77	ø	6.45	5.99
l see a s	(59.3)	(4.4)			1486s	1260s	9208	906m				
$Na_{3}[W_{2}O_{5}(esc)_{2}] \cdot 2H_{2}O_{5}(esc)_{2}] \cdot 2H_{2}O_{5}(esc)_{2}$	24.5	1.8		5.7	1488s	1267s	899s	873s	6.20	7.95	6.90	6.70
	(24.5)	(1.4)		(5.2)	1504s	1270m	904m	880w				
trans-[UO <sub>2</sub> (esc) · MeOH]	25.3	1.7			1488s	1263s		930s	5.80	7.71	6.30	6.20
	(25.1)	(1.7)			1480s	1260s	8515					
K,[OsO <sub>2</sub> (esc) <sub>2</sub> ] · 2H <sub>2</sub> O	31.5	1.6		$11.2^{b}$	1482s	1258s		826s	6.25	8.05	7.20	7.05
	(31.4)	(1.7)		(11.3)	14825	1256s	870s					
$(PPh_4)_2[Os(esc)_3]$	64.3	3.7			1497s	1265s			5.35	6.90	6.45	5.98
and the second se	(64.5)	(3.8)			1482s	1252s						

Table 1. Analytical and spectroscopic data of esculetin and its complexes

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$(PPh_4)_2[Ir(esc)_3] \cdot H_2O$	63.1	3.7		1495s	1265s		5.47	7.48	6.48	5.93
	(63.6)	(3.8)		1512s	1268s					
$(PPh_4)_2[Re(esc)_3]$	64.3	4.1		1497s	1265s		6.05	ø	6.88	6.71
	(64.6)	(3.8)		1500s	1260m					
[ReOI(PPh <sub>3</sub> ) <sub>2</sub> (esc)]	52.3	3.2		1481s	1255s	952°	5.48	7.49	6.46	5.94
	(52.5)	(3.3)								
[Pd(PPh <sub>3</sub> ) <sub>2</sub> (esc)]	66.8	4.0		1481s	1253s		5.76	a	60.9	5.90
	(0.0)	(4.2)		1484s	1260s					
$[Pt(PPh_3)_2(esc)]$	60.3	3.8		1481s	1254s		5.85	7.66	6.26	6.03
	(60.3)	(3.8)		1481s	12585			×		
$[Pd(bipy)(esc)] \cdot 2H_2O$	48.3	3.0	5.9	1487s	1256s		5.90	7.71	6.46	6.32
	(48.1)	(3.4)	(5.9)	1490s	1254s					
[Pt(bipy)(esc)] • 5H <sub>2</sub> O	37.1	3.4	4.9	1467s	1258s		5.85	7.42	6.61	6.53
	(37.0)	(3.6)	(4.5)							
[Co(en) <sub>3</sub> ][Rh(esc) <sub>3</sub> ]	45.9	4.1	9.7	1484s	1258s					
and the second se	(45.5)	(4.2)	(1.6)							
$[Co(en)_3][Fe(esc)_3] \cdot 2H_2O$	46.1	5.1	9.8	1482s	1260s					
	(46.1)	(4.7)	(8.6)							
[Ru(bipy)(esc) <sub>2</sub> ]	54.5	2.9	4.8	1480s	1260s					
	(55.2)	(2.7)	(4.6)							
<sup><i>a</i></sup> <sup>1</sup> H NMR band interferes with the <sup><i>b</i></sup> K analysis. <sup><i>c</i></sup> v(Re—O).	e phenyl ring	3; d = do	ublet, s = single	et. Raman data ir	i talics.					

Complexes of esculetin

3400 cm<sup>-1</sup> and the deformation vibration  $\delta$ (OH) at 1400 cm<sup>-1</sup> of the free ligand are not observed in the complexes, while bands at 1480 and 1260  $cm^{-1}$ probably arise from ring  $v(C-C)^{14}$  and v(C-O)modes, respectively. As expected the v(C=O) stretch of free esculetin is unaffected by coordination. In addition to the bands attributed to esculetin, the oxo-molybdenum and -tungsten complexes show bands attributed to cis-MO<sub>2</sub> stretches. Strong Raman bands near 920 cm<sup>-1</sup> which are weak in the IR are assigned to the symmetric  $v_s(MO_2)$  stretch while the weak Raman bands near 900  $cm^{-1}$ , strong in the IR, are assigned to the asymmetric  $v_{as}(MO_2)$  stretch of the cis-MO<sub>2</sub> moiety. The complexes  $[M_2O_5(cat)_2]^{2-1}$ (M = Mo, W) are known to contain a bridging oxoligand<sup>2</sup> and like these  $[M_2O_5(esc)_2]^{2-}$  has an IR band near 725 cm<sup>-1</sup> assigned to  $v_{as}(M_2O)$ . Both trans-UO<sub>2</sub>(esc) · MeOH and  $[OsO_2(esc)_2]^{2-}$  complexes show strong IR bands not observed in the Raman at 930 and 830 cm<sup>-1</sup>, respectively, assigned to  $v_{as}(MO_2)$  of the trans-O=M=O moiety while the strong Raman bands at 851 and 870 cm<sup>-1</sup>, respectively, are assigned to the symmetric stretch  $v_s(MO_2)$ ; in accordance with the likely trans geometry; these bands are very weak in the IR. 2,8,9,14,15

# (3) <sup>1</sup>H and <sup>13</sup>C NMR spectra

The <sup>1</sup>H NMR spectrum of esculetin in  $(C^{2}H_{3})_{2}SO$  (Table 1) is in close agreement with the published data.<sup>16</sup> The H<sub>3,4</sub> protons appear as a doublet at  $\delta$  6.15 and 7.85 ppm, respectively, while H<sub>5,8</sub> appear as singlets at  $\delta$  6.96 and 6.73 ppm, respectively; protons of the hydroxy groups appear as a broad singlet at  $\delta$  9.8 ppm in the ligand but are not observed in the complexes. In the latter the resonances arising from H<sub>5,8</sub> shift to higher

field probably due to the decrease of electronic density in the aromatic ring caused by coordination to the metal.<sup>17</sup>

The  ${}^{13}CNMR$  spectrum of esculetin in  $(C^2H_3)_2SO$ has been measured and assigned and our spectrum (Table 2) agrees with the published data: $^{18-21}$ the <sup>13</sup>C NMR of the complexes sufficiently soluble in <sup>2</sup>H<sub>2</sub>O and (C<sup>2</sup>H<sub>3</sub>)<sub>2</sub>SO are also listed in Table 2. It is found that the carbon atoms adjacent to the oxygen donor atoms ( $C_6$  and  $C_7$ ) shift downfield (similar effects are observed for catecholato,<sup>2,4</sup> naphthalene-2,3-diolato,<sup>8</sup> catecholamine,<sup>9</sup> tropo-lonato and maltolato<sup>15</sup> complexes). The shifts to lower field observed for C2,, C4 and C9 may arise from weak interaction of the carbonyl and pyranone oxygen atoms to the metal or to the weak hydrogen-bonding in solution. Consistent with this is our observation (Table 2) that these resonances are shifted slightly downfield when the <sup>13</sup>C spectrum of free esculetin in pure (C<sup>2</sup>H<sub>3</sub>)<sub>2</sub>SO is compared with its spectrum in a 2:1 ( $C^2H_3$ )<sub>2</sub>SO:  $^2H_2O$  solution; in the latter increased hydrogen-bonding effects are likely to be operative.

#### (4) Cyclic voltammetry

The cyclic voltammogram (CV) of esculetin in dimethylsulphoxide shows two one-electron reduction waves at -0.45 and -1.3 V (all potentials are quoted vs the Cp<sub>2</sub>Fe<sup>+</sup>/Cp<sub>2</sub>Fe couple as arbitrary zero). The first is reversible and may correspond to radical anion formation while the second is irreversible (similar features are observed in coumarin<sup>22</sup>); there is an irreversible two-electron oxidation wave at +1.1 V which could arise from oxidation of the catecholato moiety.<sup>23</sup>

The CV of  $(PPh_4)_2[Os(esc)_3]$  in acetonitrile gives an irreversible one-electron reduction wave at -0.8V which may arise from reduction of osmium(IV)

Compound	C,	C <sub>3</sub>	C₄	C,	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C。	C <sub>10</sub>
	+ 				·····	· · · · · · · · · · · · · · · · · · ·			
H <sub>2</sub> esc <sup>a</sup>	160.5	111.3	144.1	112.3	142.7	150.2	102.5	148.4	110.6
$H_2 esc^b$	163.4	112.4	145.9	113.5	143.4	150.8	103.7	149.5	112.2
$Na_2[MoO_2(esc)_2] \cdot H_2O$	168.8	111.5	153.4	112.5	149.8	165.1	103.6	156.9	110.6
$(Et_4N)_2[Mo_2O_5(esc)_2] \cdot 4H_2O$	168.7	111.6	145.6	112.5	149.9	165.2	103.6	156.2	110.7
$Na_2[W_2O_5(esc)_2] \cdot 2H_2O$	168.6	111.8	153.4	112.9	149.7	164.3	104.5	156.2	111.0
$(Et_4N)_2[WO_2(esc)_2] \cdot 5H_2O$	168.7	112.4	153.6	113.0	149.9	165.1	104.7	153.6	111.1
trans-[UO2(esc) · MeOH]"	171.7	113.6	144.5	112.5	149.7	161.9	104.6	151.2	111.6
$trans-K_2[OsO_2(esc)_2] \cdot 2H_2O$	168.6	113.3	152.8	114.6	149.3	165.7	104.8	153.2	111.9

Table 2. <sup>13</sup> C NMR of esculetin and some of its complexes

 $^{a}(C^{2}H_{3})_{2}SO.$ 

 ${}^{b}2:1(C^{2}H_{3})_{2}SO:{}^{2}H_{2}O.$ 

<sup>13</sup>C NMR of the complexes have been run in  ${}^{2}H_{2}O$ .

to osmium(III) and two irreversible one-electron oxidation waves at +1.33 and +1.45 V from oxidation of osmium(IV) to osmium(V) and osmium(V) to osmium(VI), respectively. For  $(PPh_4)_2$ [Re(esc)<sub>3</sub>] in acetonitrile we found a reversible one-electron reduction wave at -0.25 V (with  $\Delta E = 90$  mV) probably arising from the reduction of rhenium(IV) to rhenium(III) and an irreversible reduction wave at -0.65 V corresponding to the reduction of rhenium(III) to rhenium(II), while an irreversible oxidation wave was also observed at +1.66 V presumably from the oxidation of rhenium(IV) to rhenium(V). The complex  $(PPh_4)_2[Ir]$  $(esc)_{3}$   $\cdot$   $H_{2}O$  shows two irreversible one-electron reduction waves at -1.0 and -1.63 V, probably from the reduction of iridium(IV) to iridium(III) and iridium(III) to iridium(II), respectively, while an irreversible oxidation wave was observed at +1.69 V due to the oxidation of iridium(IV) to iridium(V). The CV of [Ru(bipy)(esc)<sub>2</sub>] in dimethylsulphoxide showed a reversible one-electron reduction wave at -0.28 V (with  $\Delta E = 30$ mV) and an irreversible wave at -0.57 V may be due to ruthenium(IV)/ruthenium(III) and ruthenium(III)/ruthenium(II) reduction. A one reversible one-electron oxidation wave at +0.5 V (with  $\Delta E = 60$  mV) and an irreversible one at +0.65 V may arise from the oxidation of ruthenium(IV) to ruthenium(V) and ruthenium(V) to ruthenium(VI), respectively. The cyclic voltammogram of Pd (bipy)(esc) in dimethylsulphoxide showed two irreversible oxidation waves at +0.48 and +0.6V, which may arise from the oxidation of palladium(II) to palladium(III) and palladium(III) to palladium(IV), respectively.

# (5) Mass spectra

We have determined the mass spectra of the neutral complexes  $M(PPh_3)_2(esc)$  (M = Pd, Pt) and Pd(bipy)(esc) using fast-atom bombardment (FAB+). The fragmentation patterns indicated the formation of the molecular ions  $[M(PPh_3)_2(esc)]^+$  (M = Pd, Pt) and  $[Pd(bipy)(esc)]^+$ . The peaks also indicated stepwise ligand loss to  $[M(PPh_3)_2]^+$ ,  $[M(PPh_3)]^+$  (M = Pd, Pt) and  $[Pd(bipy)]^+$ . The mass spectrum of the complex  $(PPh_4)_2[Os(esc)_3]$  was determined using (FAB-) conditions in which peaks due to  $[Os(esc)_3]^-$  and  $[Os(esc)_2]$  were observed.

#### **EXPERIMENTAL**

### $Cis-Na_2[MoO_2(esc)_2] \cdot 2H_2O$

Sodium molybdate  $Na_2[MoO_4]$  (0.24 g, 1 mmol) in water (5 cm<sup>3</sup>) was added to esculetin (0.18 g, 1 mmol) in ethanol (5 cm<sup>3</sup>). A brown solution appeared followed by a red-brown precipitate. It was filtered off, washed with ethanol, diethyl ether and dried *in vacuo*.

# $(PPh_4)_2[MoO_2(esc)_2] \cdot 4H_2O$ and $(Et_4N)_2[Mo_2O_5(esc)_2] \cdot 5H_2O$

Ammonium molybdate  $(NH_4)_2[MOO_4]$  (0.24 g, 1 mmol) in water (2 cm<sup>3</sup>) was added to esculetin (0.18 g, 1 mmol) in water (10 cm<sup>3</sup>) and tetraphenylphosphonium chloride (0.76 g, 2 mmol) in water (5 cm<sup>3</sup>) was added to the resulting red solution. A yellow precipitate was produced, filtered off, washed with water and dried *in vacuo*.

The tetraethylammonium salt was isolated by adding tetraethylammonium chloride (0.34 g, 2 mmol) in water  $(5 \text{ cm}^3)$  to the red solution of the latter preparation. The volume of the red solution was reduced until the yellow-green precipitate was formed.

Cis-Y<sub>2</sub>[W<sub>2</sub>O<sub>5</sub>(esc)<sub>2</sub>]  $\cdot$  nH<sub>2</sub>O (Y = Na, n = 2; Y = Et<sub>4</sub>N, n = 5)

A similar procedure as for the molybdenum analogue was used, sodium tungstate replacing ammonium or sodium molybdate and producing yellow precipitates of the products.

 $Cis-(PPh_4)_2[WO_2(esc)_2] \cdot 5H_2O$ 

Sodium tungstate (0.33 g, 1 mmol) in water  $(2 \text{ cm}^3)$  was added to esculetin (0.18 g, 1 mmol) in water  $(10 \text{ cm}^3)$ . Tetraphenylphosphonium chloride (0.76 g, 2 mmol) in water  $(5 \text{ cm}^3)$  was added to the resulting yellow solution. The yellow solution was reduced in volume until a yellow precipitate separated out. This was filtered off, washed with a little water and dried *in vacuo*.

#### Trans-UO<sub>2</sub>(esc) · MeOH

Uranyl acetate  $UO_2(CH_3COO)_2 \cdot 2H_2O$  (0.21 g, 0.5 mmol) in methanol (5 cm<sup>3</sup>) was added to a solution of esculetin (0.09 g, 0.5 mmol) in methanol (5 cm<sup>3</sup>). The brown mixture was refluxed for 2 h on a steam bath. Upon reducing the volume a brown precipitate separated out. It was washed with methanol, ether and dried *in vacuo*.

 $Trans-K_2[OsO_2(esc)_2] \cdot 2H_2O$ 

Potassium osmate  $trans-K_2[OsO_2(OH)_4]$  was prepared by the literature method.<sup>24</sup> Trans-K<sub>2</sub> [OsO<sub>2</sub>(OH)<sub>4</sub>] (0.1 g, 0.25 mmol) in water (2 cm<sup>3</sup>) was added to a solution of esculetin (0.09 g, 0.5 mmol) in ethanol (3 cm<sup>3</sup>) with stirring. The dark brown solution was left to stand for 30 min after which time a brown precipitate was filtered off and dried *in vacuo*.

# $(Ph_4P)_2[OsO_2(esc)_2] \cdot 5H_2O$

The potassium salt  $K_2[OsO_2(esc)_2] \cdot 2H_2O$  in water (5 cm<sup>3</sup>) and tetraphenylphosphonium chloride were mixed in a 2:1 molar ratio, whereupon a fine brown-violet precipitate appeared. It was filtered off, washed with water and dried *in vacuo*.

# $(PPh_4)_2[Os(esc)_3]$

Sodium hexachloro-osmate (0.15 g, 0.33 mmol) and esculetin (0.18 g, 1 mmol) were dissolved in water (3 cm<sup>3</sup>) and the brown suspension degassed with nitrogen. Sodium hydroxide (0.08 g, 2 mmol) in water (2 cm<sup>3</sup>) was degassed and added to the suspension. The solution immediately became brown. It was left to stand for 30 min and tetraphenylphosphonium chloride (0.25 g, 0.66 mmol) in water (5 cm<sup>3</sup>) added. A green-brown precipitate was formed. After standing for 2 h, the solid was filtered off, washed with water and dried under a stream of nitrogen, then over concentrated sulphuric acid.

## $(PPh_4)_2[Ir(esc)_3] \cdot H_2O$

A similar method to that for the osmium complex  $(PPh_4)_2[Os(esc)_3]$  was used, with  $Na_2[IrCl_6]$  replacing  $Na_2[OsCl_6]$ .

# $(PPh_4)_2[Re(esc)_3]$

A similar method to that for the osmium complex  $(PPh_4)_2[Os(esc)_3]$  was used, with  $K_2[ReCl_6]$  replacing Na<sub>2</sub>[OsCl<sub>6</sub>].

## [ReOI(PPh<sub>3</sub>)<sub>2</sub>(esc)]

The complex  $[\text{ReO}_2\text{I}(\text{PPh}_3)_2]$  was prepared by the literature method.<sup>25</sup> A suspension of  $[\text{ReO}_2\text{I}(\text{PPh}_3)_2]$  (0.22 g, 0.25 mmol) in methanol (15 cm<sup>3</sup>) was stirred and heated gently with the addition of esculetin (0.09 g, 0.5 mmol). The mixture was warmed and stirred for about 1 h, after which time a brown precipitate was isolated, washed with methanol and dried *in vacuo*.

#### $[M(PPh_3)_2(esc)] (M = Pd, Pt)$

Both cis-[Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>26</sup> and cis-[Pt(PPh<sub>3</sub>)<sub>2</sub> Cl<sub>2</sub>]<sup>27</sup> were prepared by the literature method.<sup>28</sup> A suspension of [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (0.7 g, 1 mmol) or [Pt(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (0.82 g, 1 mmol) in ethanol (20 cm<sup>3</sup>) was added to a methanolic solution containing esculetin (0.18 g, 1 mmol) and KOH (0.11 g, 2 mmol) and the mixture was stirred overnight at room temperature. A green (palladium) or yellow (platinum) precipitate was isolated, washed with methanol, water, methanol, ether and dried *in vacuo*.

 $[M(bipy)(esc)] \cdot nH_2O \quad (M = Pd, n = 2; M = Pt, n = 5)$ 

The complexes  $[M(bipy)Cl_2]$  (M = Pd, Pt) were prepared by a modification of the literature method<sup>29,30</sup> in which to K<sub>2</sub>[PdCl<sub>4</sub>] (0.32 g, 1 mmol) or  $K_2[PtCl_4]$  (0.42 g, 1 mmol) in water (5 cm<sup>3</sup>) was added 2,2'-bipyridyl (0.16 g, 1 mmol) in 2 M HCl  $(15 \text{ cm}^3)$ . The resulting solution was allowed to stand at 70-80°C in a water bath for 3 h to produce orange (palladium) or yellow (platinum) fine crystalline needles, which were washed with water and dried in vacuo. Then [Pd(bipy)Cl<sub>2</sub>] (0.17 g, 0.5 mmol) or [Pt(bipy)Cl<sub>2</sub>] (0.21 g, 0.5 mmol) was dissolved in dimethyl formamide (15 cm<sup>3</sup>) and silver nitrate (0.17 g, 1 mmol) was added. The mixture was heated in a water bath for 1 h in the dark. The precipitate of AgCl was removed by filtration and the filtrate mixed with benzene (60 cm<sup>3</sup>) and kept for 3 h in a refrigerator. The yellow (palladium) or brown (platinum) precipitate thus obtained was extracted with water  $(30 \text{ cm}^3)$ . To this aqueous solution a solution of esculetin (0.11 g, 0.6 mmol) and NaOH (0.05 g, 1.2 mmol) in water  $(5 \text{ cm}^3)$  was added. An orange-brown (palladium) or deep brown (platinum) precipitate was obtained; it was filtered off, washed with water and dried in vacuo.

#### $[Co(en)_3][Rh(esc)_3]$

Hydrated rhodium trichloride (0.14 g, 0.45 mmol) was added to a solution of sodium acetate (1.05 g, 0.7 mmol) in water (25 cm<sup>3</sup>) and heated gently while esculetin (0.27 g, 1.5 mmol) was added with stirring. The reaction mixture was refluxed for 6 h during which time it turned red-orange. It was left to cool, after which a solution of  $[Co(en)_3]Cl_3$  (0.18 g, 0.45 mmol) in water (2 cm<sup>3</sup>) was added. A yellow-orange precipitate was produced, filtered off, washed with water and dried *in vacuo*.

# $[Co(en)_3][Fe(esc)_3] \cdot 2H_2O$

Hydrated ferric chloride (0.09 g, 0.33 mmol) in water (5 cm<sup>3</sup>) was added to esculetin (0.18 g, 1 mmol) and KOH (0.11 g, 2 mmol) in water (5 cm<sup>3</sup>).  $[Co(en)_3]Cl_3$  (0.12 g, 0.33 mmol) in water (2 cm<sup>3</sup>) was added to the red solution. A deep brown precipitate was isolated, washed with water and dried *in vacuo*.

#### [Ru(bipy)(esc)<sub>2</sub>]

[Ru(bipy)Cl<sub>3</sub>] was prepared by the literature method.<sup>31</sup> All the manipulations were carried out under nitrogen. To degassed methanol (15 cm<sup>3</sup>), [Ru(bipy)Cl<sub>3</sub>] (0.18 g, 0.5 mmol) and esculetin (0.18 g, 1 mmol) were added. The resultant reaction mixture was refluxed for half an hour. The addition of a solution of NaOH (0.08 g, 2 mmol) in methanol (8 cm<sup>3</sup>) gave a brown solution which was refluxed for 24 h. After cooling the brown solution to room temperature, the mixture was exposed to air, upon which the deep brown microcrystalline products were isolated.

Raman spectra were measured at 100 mW using the 6471 Å line on a krypton or 5145 Å on an argon ion laser with a Spex Ramalog V instrument and Spex Datamate data acquisition unit, as spinning discs with a KBr base. IR spectra were measured on a Perkin–Elmer 1720 Fourier-transform spectrometer. NMR spectra were measured on a Bruker WM–250 spectrometer. Cyclic voltammograms were measured with an Oxford Electrodes PVSU potentiostat and Houston Instruments Omnigraphic 2000 recorder. Mass spectra were run by the Organic Mass Spectroscopy Laboratory, Imperial College, and microanalyses were carried out by the Microanalytical Department, Imperial College.

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