Synthesis and Characterization of Ruthenium(II) Complexes of 5-Hydroxyflavones

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Bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) complexes, $RuL_2(DMSO)_2$, were synthesized by the reaction of dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) with the sodium salts of 5-hydroxyflavone, 5-hydroxy-4'-methoxyflavone and 5-hydroxy-3',4',5',7-tetramethoxyflavone, (L). The complexation was followed by ^{1}H nmr spectroscopy. The 1:1 kinetically favoured tris(dimethyl sulfoxide)chloroflavonatoruthenium(II) complexes, $RuLCl(DMSO)_3$, were initially formed and then transformed into the thermodynamically more stable ones. Each one of these complexes, by reacting with another equivalent of ligand L, also gave rise to a mixture of 1:2 kinetic species, from which the 1:2 thermodynamically more stable bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) complexes, $RuL_2(DMSO)_2$, were formed. The complexes were characterized by extensive studies involving ^{1}H, ^{13}C nuclear magnetic resonance, infrared and ultraviolet-visible spectroscopy, mass spectrometry, cyclic voltammetry and elemental analysis. Such 1:2 complexes exhibited properties of two nonequivalent flavonate ligands and also of two non-equivalent dimethyl sulfoxide ligands; one of these dimethyl sulfoxide ligands is considered to be S-bonded and the other O-bonded. Also two quasireversible one-electron redox steps were observed at 0.53 to 0.57 and 0.44 to 0.41 V (vs Saturated Calomel Electrode). The spectroscopic results obtained allow for the discussion of stereochemistry of each bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) complex and to postulate its possible structure as one corresponding to the more anisochronous species.

Introduction.

Natural flavones are a group of phenolic derivatives widely occuring in all vegetal sources. Such compounds can be found in leaves, wood, fruits, and flowers. The flavones and other similar compounds possess a variety of biological functions [1-9]. These include the protection of the living plant from ultraviolet radiation, and from certain insects and infections by acting as biocides. Flavones also act as attractants for the pollinator insects, as enzyme inhibitors, allelopathic agents, antioxidants, *etc*. Such biological activities can be mimicked *in vitro* by using natural or synthetic flavones. Applications of these compounds as agrochemicals [10-12], new drugs [13-16] and antioxidants [17,18] have been suggested for such compounds. In particular, the antioxidant activity is basically a function of their abilities to act as free radical scavengers and also to remove some metal ions by complexation [17,19-22]. In this way a certain flavone derivative being present in a food product to be eaten may inhibit some cancer and inflammatory disorders and cellular damage, such as rheumatoid arthritis. These potential new applications for such compounds are very promising. It is then desirable to increase the chemical knowledge about flavones and flavone metal complexes which may be formed from 5-hydroxyflavones and biologically significant metal ions.
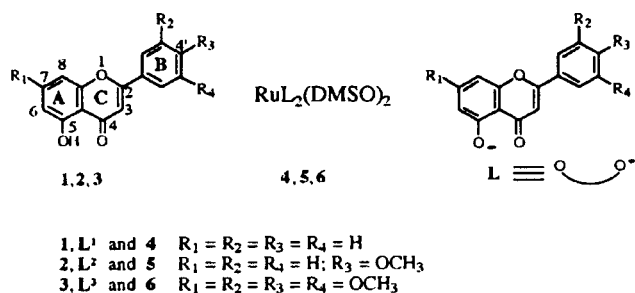
It has been shown that 5-hydroxyflavones can be used, as ligands, in the spectrophotometric determinations of

several metal ions [23-25]. However, the structural characterization of the complexes, particularly those obtained with transition metal ions, has been only reported in a few cases [26]; these studies have been carried out with the participation of paramagnetic metal centers. Complexation studies of that type have not yet included the use of ruthenium(II) ions.

Fortunately, the diamagnetic properties of such ruthenium(II) species will allow the use of nuclear magnetic resonance spectroscopy in the structure elucidation of the new complexes; with such technique it is also possible to follow the complexation processes. It is known that some ruthenium(II) octahedral complexes show interesting properties, as catalysts, in solar energy conversion [27-30], in the selective sulfide oxidation [31] by dioxygen and in the hydrogenation of α,β-unsaturated ketones and amides [32,33]. Some possible medicinal uses for other ruthenium(II) complexes have also been put forward [34-36]. One can then envisage that other useful applications may be exhibited by other ruthenium(II) complexes if they are made available.

In this paper we report the synthesis and characterization (mainly by ^{1}H and ^{13}C nuclear magnetic resonance, mass spectrometry and elemental analysis) of the novel bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II). The complexation processes, in tetradeuteriomethanol, were also followed by nuclear magnetic resonance spectroscopy. The complexes were obtained from the reaction

of dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) with the appropriate flavone anions. These were prepared from the following flavones: 5-hydroxyflavone, (**1**), 5-hydroxy-4'-methoxyflavone, (**2**), and 5-hydroxy-3',4',5',7-tetramethoxyflavone, (**3**). The following aspects were taken into consideration in the use of such flavones: (**1**), the simplest of the three compounds, can represent a model for that type of anion ligand; the other two compounds, (**2**) and (**3**), allow for an easier interpretation of the nmr spectra of the new complexes and of those taken during the complexation processes.

1,2,3   4,5,6   L ≡

1. L¹ and 4   R₁ = R₂ = R₃ = R₄ = H
2. L² and 5   R₁ = R₂ = R₄ = H; R₃ = OCH₃
3. L³ and 6   R₁ = R₂ = R₃ = R₄ = OCH₃

Results and Discussion.

Synthesis and Characterization.

Treatment of dichlorobis(dimethyl sulfoxide)ruthenium(II) with two molar equivalents of each ligand anion L obtained from the corresponding 5-hydroxyflavones **1-3** as described before, gave the bis(dimethyl sulfoxide)bis-(flavonato)ruthenium(II) complex, $RuL_2(DMSO)_2$.

The positive FAB mass spectra obtained for the three complexes clearly show the formation of the molecular ions $[RuL_2(DMSO)_2]^{+\cdot}$ at m/z 732, 792 and 972 respectively for bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) (**4**), bis(dimethyl sulfoxide)bis(4'-methoxyflavonato)ruthenium(II) (**5**) and bis(dimethyl sulfoxide)bis-(3',4',5',7-tetramethoxyflavonato)ruthenium(II) (**6**); also the formation of ions $[RuL_2(DMSO)_2-(DMSO)_2]^{+\cdot}$ in each case can be observed at m/z 576, 636 and 816. Ions $[LH+H]^+$ are also present at m/z 239, 269 and 359.

The cyclic voltammetry experiments were run at moderate sweep rate (0.2 - 0.5 Vs⁻¹), and from the obtained results it is possible to see that each complex exhibits quasireversible one-electron processes of oxidation and reduction which are related with the metal center. The oxidation (0.53 - 0.57 V) and reduction (0.41 - 0.44 V) potentials are not significantly affected by the type of substituents present in the flavonate ligands.

¹H and ¹³C NMR Spectroscopy.

The chemical shifts and coupling constants for 5-hydroxyflavone (**1**), 5-hydroxy-4'-methoxyflavone (**2**) and

5-hydroxy-3',4',5',7-tetramethoxyflavone (**3**), flavonate (L^1), 4'-methoxyflavonate (L^2) and 3',4',5',7-tetramethoxyflavonate (L^3) and their corresponding ruthenium(II) complexes bis(dimethyl sulfoxide)bis(flavonato)-ruthenium(II) (**4**), bis(dimethyl sulfoxide)bis(4'-methoxyflavonato)ruthenium(II) (**5**) and bis(dimethyl sulfoxide)bis(3',4',5',7-tetramethoxyflavonato)ruthenium(II) (**6**), are shown in Tables 1 and 2.

The assignments of all protons and carbons have been made by considering the available literature data for flavones [17,41-46] and also from two dimensional experiments (HETCOR) for protons and the proton-coupled ¹³C nmr spectra for carbons.

As is shown in Table 1, the nmr signal due to H-8 of each ligand L has a shift to lower frequency (0.5 to 0.6 ppm) in comparison with the corresponding signal of the 5-hydroxyflavone derivative (from which such ligand was obtained). The same behaviour is observed with H-6 and H-7, although to a smaller degree (0.26 to 0.36 ppm). These shifts can be rationalized by considering the electronic effects on all protons of the aromatic ring A due to the charge of the anion, which most strongly affects the *para* position.

An analogous situation is observed for H-3. The 5-hydroxyflavones have a strong hydrogen bond involving the carbonyl and the proton of the 5-hydroxyl groups, inducing a delocalization along the α,β-unsaturated keto part of the molecule. In the anionic form L such a hydrogen bond does not exist and, as a consequence, the delocalization effect is decreased and H-3 is shielded (0.1-0.2 ppm).

Upon complexation the ring B protons are not significantly affected, a situation which is not true for those of rings A and C. In fact, by comparison with the flavonate protons, H-3, H-6 and H-8 are deshielded in the complexes (0.1-0.3 ppm for H-3 or H-8 and 0.3-0.4 ppm for H-6). It can be suggested that the complexation is a process which increases the delocalization along the α,β-unsaturated keto moiety and decreases the electronic density around the proton atoms on ring A. Also for each complex two additional factors have to be considered, namely the σ donor effect from the ligand to the metal ion and the π-back bonding from the metal ion to the ligand. The former effect is responsible for a distance-dependent deshielding situation on the protons of the ring A, particularly for H-6. The latter gives a shielding contribution for the resonances of the protons of ring A, which is especially important for the *para* -position (H-8). Since the σ donor effect is stronger than that for the π-back bonding, the overall processes correspond to shifts to higher frequencies in the ¹H nmr spectra.

As shown in Table 2, similar effects are observed in the ¹³C nmr spectra of the three flavones, their flavonates and the corresponding ruthenium(II) complexes.

Table 1

[1]H Chemical Shifts [a], (ppm from tetramethylsilane), of the 5-Hydroxyflavones
1,2 and 3, of their Flavonates L^1,L^2 and L^3 and of the corresponding
Bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) complexes 4, 5, and 6 [b]

Compound	OH-5	3	6	7	8	2',6'	3',5'	4'
1	12.58	6.74	6.82	7.55	7.00	7.91	7.54	7.54
	(s)	(s)	(d, 8.2)	(t, 8.4)	(d, 8.4)	(d, 7.6)	(m)	(m)
L^1		6.57	6.46	7.27	6.45	7.95	7.55	7.55
		(s)	(d, 8.6)	(t, 8.2)	(d, 8.2)	(m)	(m)	(m)
4		6.72	6.74	7.29	6.56	7.81	7.43	7.43
		6.90	6.85		6.59	7.93	7.52	7.52
		(s)	(d, 7.4)	(t, 8.3)	(d, 8.3)	(d, 7.4)	(m)	(m)
2	12.66	6.65	6.80	7.52	6.98	7.87	7.02	3.90
	(s)	(s)	(d, 9.3)	(t, 9.0)	(d, 9.0)	(d, 9.5)	(d, 9.5)	(OCH$_3$)
L^2		6.49	6.45	7.26	6.44	7.90	7.09	3.89
		(s)	(d, 8.5)	(t, 8.1)	(d, 8.1)	(d, 9.0)	(d, 9.0)	(OCH$_3$)
5		6.62	6.71	7.26	6.52	7.75	6.91	3.82
		6.80	6.82		6.55	7.86	7.01	3.89
		(s)	(d, 7.9)	(t, 7.8)	(d, 7.8)	(d, 8.5)	(d, 8.5)	(OCH$_3$)
3	12.71	6.58	6.36	3.93	6.49	7.07	3.95	3.88
	(s)	(s)	(d, 2.2)	(OCH$_3$)	(d, 2.2)	(s)	(OCH$_3$)	(OCH$_3$)
L^3		6.45	6.09	3.83	6.03	7.17	3.93	3.79
		(s)	(d, 2.2)	(OCH$_3$)	(d, 2.2)	(s)	(OCH$_3$)	(OCH$_3$)
6		6.62	6.34	3.88	6.19	7.02	3.89	3.75
		6.75	6.42	3.94	6.20	7.09	3.97	3.84
		(s)	(d, 2.2)	(OCH$_3$)	(d,2.2)	(s)	(OCH$_3$)	(OCH$_3$)

[a] In brackets is shown the multiplicity of each signal and the corresponding coupling constant (J, Hz). [b] Chemical shifts for the methyl groups of the two dimethyl sulfoxide ligands are: 2.89,3.23, 3.31 and 3.35 in complex 4; 2.87, 3.21, 3.25 and 3.33 in 5; 2.90, 3.20, 3.32 and 3.35 in 6.

Table 2

[13]C Chemical Shifts [a], (ppm from tetramethylsilane), of the 5-Hydroxyflavones 1,2 and 3 their Flavonates L^1,L^2 and L^3 and
Corresponding Bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) complexes 4,5 and 6

Compound	2	3	4	5	6	7	8	9	10	1'	2',6'	3',5'	4'
1	164.6	106.0	183.6	160.8	111.4	135.4	107.1	156.4	110.9	131.2	126.4	129.1	132.1
L^1	161.8	107.8	182.7	173.1	118.1	135.1	99.3	160.2	115.7	132.8	126.7	129.9	132.1
4	167.8	105.6	179.7	159.5	118.2	133.8	100.3	157.9	113.2	131.2	126.1	128.9	131.4
	169.3	106.7	182.4	160.7	118.8	134.7	100.4	158.2	113.4	131.2	126.2	129.1	131.6
2	164.5	104.5	183.4	160.3	111.3	135.1	106.9	156.3	110.7	123.4	128.1	114.5	162.7
L^2	162.0	106.3	182.9	172.9	118.0	135.0	99.4	160.1	115.5	124.9	128.5	115.3	163.1
5	166.6	103.3	178.6	158.6	117.0	132.6	99.2	156.9	112.0	122.4	126.9	113.3	161.2
	168.2	104.4	181.2	159.7	117.7	133.4	99.3	157.1	112.2	122.5	126.9	113.5	161.4
3	163.8	105.6	182.3	162.2	98.2	165.6	92.7	157.7	103.7	126.5	103.7	153.6	141.4
L^3	161.1	107.7	181.7	174.3	101.9	166.2	88.0	161.3	111.1	128.6	104.4	154.6	141.4
6	169.1	105.3	178.1	159.3	108.3	164.6	90.1	158.9	101.1	126.5	103.3	153.4	140.7
	170.4	106.2	180.6	159.9	108.5	165.2	90.2	159.0	102.0		103.4	153.6	140.9

[a] Chemical shifts for the carbon methyl groups of the two dimethyl sulfoxide ligands: 42.3, 43.8, 43.8 and 44.1 in complex 4; 41.3, 42.8, 42.9 and 43.1 in 5; 42.4, 43.9, 43.9 and 44.2 in 6. For the methoxyl substituents, the chemical shifts are as follows: 55.8, 55.5 and 55.4 ppm for the 7-OCH$_3$ and 56.4, 56.9 and (56.3, 56.4) ppm for the 3',5'-di-OCH$_3$ of 3, L^3 and 6; 55.5, 56.0, (54.5, 54.6), 61.1, 61.2 and 61.0 for the 4'-OCH$_3$ of 2, L^2, 5, 3, L^3 and 6.

The anionic center present in the flavonates affects the resonances of the rings A and C carbons, while the ring B carbons are almost unaffected with the exception of C-1' which is shifted (2 ppm) to higher frequencies. In ring A, the effects on C-7 and C-9 are small. However C-5, C-6 and C-10 are shifted, respectively, by 12-13, 4-7 and 5-7 ppm to higher frequencies; C-8 is also shifted by 4-8 ppm but to lower frequencies. Such shifts can be expected if

the parallel situation in the phenol-phenoxyde case is considered [47], *i.e.*, there will be a deshielding of the *ipso* and the *ortho* and a shielding for the *para* carbon atoms.

By comparison with the C-2 and C-3 chemical shifts of flavones, the corresponding carbon atoms of flavonates have opposite shifts; C-2 is shifted (3 ppm) to lower and C-3 (2 ppm) to higher frequencies. Such effects can be attributed to the delocalization and lack of hydrogen bonding phenomena already mentioned in the ^{1}H nmr analysis.

As could be anticipated, the complexation also affects the resonances of the carbon atoms of each ligand. The major differences are found for C-2, which is deshielded by 5-9 ppm, and C-5, which is shielded by 12-15 ppm. Such differences in chemical shifts can be explained by taking into account the overall situation as a result of the previously mentioned electronic processes which will operate in each complex.

Structures of the New Complexes.

As shown in Tables 1 and 2, a set of results for each flavonate ligand has been observed in the ^{1}H and ^{13}C nmr spectra of each complex.

By considering the chemical shift values already published for other kinds of complexes, in which dimethyl sulfoxide ligands are *S*- and *O*-bonded [33,48-52], one can postulate that in this case the two ligands are linked in different ways. Also the low symmetry of each complex probably causes the non-equivalence of the two methyl groups of each *S*- and *O*-bonded dimethyl sulfoxide ligands. The methyl group ^{1}H resonances at 3.25-3.32 and 3.33-3.35 ppm may be attributed to an *S*-bonded dimethyl sulfoxide and the others at 2.87-2.90 and 3.20-3.23 ppm to an *O*-bonded species. This structural possibility is also corroborated by the results obtained by infrared spectroscopy. Although several peaks can be observed in the region 900-1100 cm^{-1} of the infrared spectrum of a 5-hydroxyflavone, other different peaks at 1008, 1092 and 1108 cm^{-1} are present in the spectrum of its ruthenium(II) complex. The absorbance at 1008 cm^{-1} can be attributed to an *O*-bonded dimethyl sulfoxide while the others at 1092 and 1108 cm^{-1} can be due to an *S*-bonded ligand [33,53]. Such spectroscopic results obtained for each complex reveal that there is a non-equivalent situation in each set of flavonates and dimethyl sulfoxide ligands.

As unsymmetrical ligands, the flavonates and the *S*- and *O*-bonded dimethyl sulfoxides, may give rise to six diastereoisomers for their ruthenium(II) complexes, five of which have enantiomers (forms **B**, **C**, **D**, **E** and **F**). Such diastereoisomers can be represented in the following way:

X = *O*-Bonded DMSO
Y = *S*-Bonded DMSO
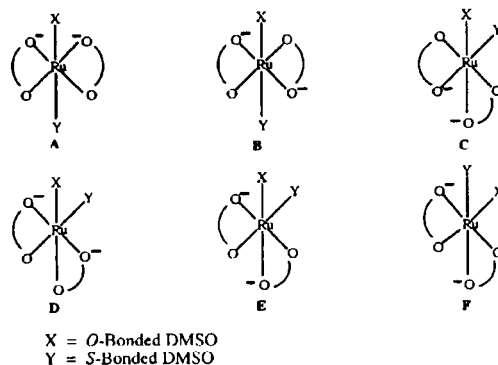
Due to its plane of symmetry the structure corresponding to form **A** is ruled out. The stuctures represented by forms **B**, **C** and **D** (or their enantiomers) are less anisochronous in comparison with the other two (forms **E** and **F**). Considering the relevant values, which can be taken from Tables 1 and 2, for the anisochrony operating in complexes bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) (**4**), bis(dimethyl sulfoxide)bis(4'-methoxyflavonato)ruthenium(II) (**5**) and bis(dimethyl sulfoxide)bis(3',4',5',7-tetramethoxyflavonato)ruthenium(II) (**6**), it is postulated that their structures can be represented by forms **E** or **F** (or their corresponding enantiomers).

Kinetic Considerations.

[1]H nuclear magnetic resonance spectroscopy was used in order to have an insight into the complexation process. Spectra were taken from reaction mixtures having ruthenium (II)/flavonate ratios of 1:1 and 1:2, in tetradeuteriomethanol.

The spectra obtained at the intermediate steps of the complexation of ligands flavonate (L^1) and 4'-methoxyflavonate (L^2) with ruthenium(II) showed a great multiplicity of signals and were difficult to interpret. However, by using 3',4',5',7-tetramethoxyflavonate (L^3) the spectral interpretation was more manageable. In fact, due to the 3',4',5'-substituted positions, the 2' and 6' aromatic protons appeared as a singlet; also the presence of the 7-methoxyl substituent in ring **A** has simplified the proton assignments of that ring.

The addition of an equivalent amount of dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) to a 3',4',5',7-tetramethoxyflavonate (L^3) solution, obtained as described before, gave an isomeric mixture of the kinetically favoured 1:1 complexes. This conclusion was based on the ^{1}H nmr spectrum of the mixture, which has displayed a group of signals shifted to higher frequencies compared to the chemical shifts of the corresponding protons in the free ligand. However, by refluxing such a mixture for five minutes, only the thermodynamically more stable tris(dimethyl sulfoxide)chloro(3',4',5',7-tetramethoxyflavonato)ruthenium(II) species can be

found. Its ^{1}H nmr spectrum showed only one signal for each 3',4',5',7-tetramethoxyflavonate (L^3) ligand proton (singlets at δ, ppm, 7.09 for H-3, 6.43 for H-6 and H-8, and 7.30 for H-2' and H-6'); also six other singlets were observed between 2.9 and 3.6 ppm, which have been assigned to the six methyl groups of the three bonded dimethyl sulfoxide molecules. No other variation was observed in this nmr spectrum when that 1:1 complex solution was refluxed for three hours. A positive FAB mass spectrum run at that stage has shown the formation of an ion at m/z 693; this value corresponds to the formation of tris(dimethyl sulfoxide)(3',4',5',7-tetramethoxyflavonato)ruthenium(II) ion, [RuL^3(DMSO)$_3$]$^+$, and to the loss of the chlorine atom. This behaviour has been already observed for other types of ruthenium complexes [54].

After the addition of a second equivalent of 3',4',5',7-tetramethoxyflavonate (L^3) to the tris(dimethyl sulfoxide)chloro(3',4',5',7-tetramethoxyflavonato)ruthenium(II) solution, the ^{1}H nmr spectrum immediately run showed the proton signals due to the free ligand 3',4',5',7-tetramethoxyflavonate (L^3) and to the tris(dimethyl sulfoxide)chloro(3',4',5',7-tetramethoxyflavonato)ruthenium(II) complex. The spectrum changed by refluxing the reaction mixture and running the spectra at different times. After five minutes, the presence of new signals could be observed and after one hour no free ligand 3',4',5',7-tetramethoxyflavonate (L^3) could be detected; however too many signals were present between 6.12 to 6.53 and 7.18 to 7.31 ppm to make the correct assignments of the corresponding protons. After refluxing the reacting solution for fifteen hours a solid product started to precipitate. This was collected after refluxing the reaction mixture for another thirty six hours; its structure has been established as being the bis(dimethyl sulfoxide)bis(3',4',5',7-tetramethoxyflavonato)ruthenium(II) (6) previously described.

EXPERIMENTAL

Measurements

The nuclear magnetic resonance spectra of the complexes, in deuteriochloroform, were recorded on AMX 300 and AC 250 Bruker spectrometers, using tetramethylsilane as internal reference. The two dimensional experiments (HETCOR) were run with a standard Bruker microprogram (HXCO), with 1024 data points for 128 increments, two dummy scans and a relaxation delay of 1.5 seconds. A non-shifted sine-bell squared function was applied to give a final matrix of 1024 x 256 points.

Fast atom bombardment mass spectra were run on a Jeol JMX DX-33 mass spectrometer, using 3-nitrobenzyl alcohol as a matrix.

Cyclic voltammograms were obtained with a Sirius apparatus connected to a 386 microcomputer. A standard three-electrode electrochemical cell was used, consisting of a working platinum electrode (ø = 1 mm), a platinum-wire auxiliary electrode and a saturated calomel reference electrode (SCE), (Tacussel XR 10). The cyclic voltammograms were recorded at a scan of 0.2-0.5 V.s^{-1} using solutions 10^{-3} M of each complex and 0.1 M of the tetrabutylammonium hexafluorophosphate in acetonitrile, at room temperature, under nitrogen. Ultraviolet-visible absorption spectra, in methanol, were recorded on a Shimadzu uv-160A spectrophotometer. Infrared spectra were recorded with a Fourier transform infrared Matson Polaris spectrometer using potassium bromide pellets. Melting points are uncorrected and were determined on a pre-heated Reichert-Thermovar hot-stage apparatus. Elemental analyses were performed by the "Service Central de Microanalyse du Centre National de la Recherche Scientifique de Montpellier".

Reagents and Synthesis.

Dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) was obtained from Johnson Matthey Alfa Products. All organic solvents were of reagent grade and have been purified by standard procedures. All the synthetic transformations were carried out under a nitrogen atmosphere. Column chromatography was carried out by using Merck silica gel (70-230 mesh ASTM). 5-Hydroxyflavone (1) was synthesized by the method of Looker [37].

Synthesis of 5-Hydroxy-4'-methoxyflavone (2) and 5-Hydroxy-3',4',5',7-tetramethoxyflavone (3).

4,6'-Dimethoxy-2'-hydroxychalcone or 3,4,4',5,6'-pentamethoxy-2'-hydroxychalcone [38] (1 mmole), in dimethyl sulfoxide (10 ml), was treated with a catalytic amount of iodine (100 mg). The reaction mixture was heated at reflux for 30 minutes; after reaching room temperature it was poured into water. The solid obtained was filtered, washed with an aqueous solution of sodium thiocyanate and dissolved in chloroform. This solution was dried (sodium sulfate) and concentrated in vacuo . The resultant residue was dissolved in acetonitrile (300 ml) and anhydrous aluminium chloride was added (13 g). This reaction mixture was heated at reflux for 10 hours; after that period it was left to reach room temperature. A 5% aqueous hydrochloric acid solution (50 ml) was then added and the mixture was heated, at 60°, for 3 hours. Water (100 ml) and chloroform (100 ml) were added. The organic phase was collected, washed with an aqueous sodium bicarbonate solution, dried (sodium sulfate) and concentrated in vacuo. The residue was dissolved in chloroform and chromatographed on a silica column, eluting with chloroform. After crystallization in ethanol, the corresponding product 5-hydroxy-4'-methoxyflavone (2) (89%, m.p. 154-156°, lit. [39] 154-156°) or 5-hydroxy-3',4',5',7-tetramethoxyflavone (3) (75%, m.p. 182-184°, lit. [40] 188-189°) was obtained.

Synthesis of Flavonate (L^1), 4'-Methoxyflavonate (L^2) and 3',4',5',7-Tetramethoxyflavonate (L^3).

5-Hydroxyflavone (1), 5-hydroxy-4'-methoxyflavone (2) or

5-hydroxy-3',4',5',7-tetramethoxyflavone (3), (0.05 mmole) in methanol (or d_4-methanol for the nmr studies), (2 ml), was treated with an equivalent amount of an aqueous 1 M sodium hydroxide solution (0.05 ml). Dimethyl sulfoxide (0.2 ml) was then added to homogenize the reaction mixture, which was then heated at reflux for 15 minutes giving a clear solution of the flavone anion.

General Procedure for the Synthesis of Bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) (4, 5 and 6).

A suspension of 5-hydroxyflavone (1), 5-hydroxy-4'-methoxyflavone (2) or 5-hydroxy-3',4',5',7-tetramethoxyflavone (3) (5 x 10^{-4} mole) in methanol (10 ml) was treated with dimethyl sulfoxide (0.5 ml) and 1 M aqueous sodium hydroxide solution (0.5 ml). The mixture was heated at reflux for 15 minutes giving a clear solution of the flavone anion. Dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) (122 mg, 2.5 x 10^{-4} mole) was then added. The resulting solution was heated at reflux (80°), with magnetic stirring, during the appropriate period of time [2, 4 or 5 days for, respectively, 5-hydroxyflavone (1), 5-hydroxy-4'-methoxyflavone (2) and 5-hydroxy-3',4',5',7-tetramethoxyflavone (3)].

Upon cooling, the complex in each case crystallized out of the reaction mixture. This solid was collected, washed with water (3 x 10 ml) and dried. The resultant liquid phases were mixed and extracted with dichloromethane (3 x 20 ml). The organic phase was dried over sodium sulfate and the solvent evaporated to dryness, giving a residue which was purified by silica gel column chromatography. Acetonitrile was used for eluting the starting material (~5%) and an unknown green product, and an acetonitrile-methanol mixture [7:3] for the bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) (4) or the bis(dimethyl sulfoxide)bis(4'-methoxyflavonato)ruthenium (II) (5). The complex bis(dimethyl sulfoxide)bis(3',4',5',7-tetramethoxyflavonato)ruthenium(II) (6) was eluted with another [7:5] acetonitrile-methanol mixture. After evaporation of the organic solvents, each complex was dissolved in dichloromethane and crystallized from petroleum ether. The crystals were collected, dried and mixed with the corresponding precipitated material mentioned above. The total yield obtained was, in each case, 70%, 63% and 66%, respectively, for 4, 5 and 6.

Bis(dimethyl sulfoxide)bis(flavonato)ruthenium(II) (4).

This compound was obtained as a dark-brown powder, mp 270-271°; uv-vis: λ max (ε) 415 (26000), 292 (99000), 250 (sh, 68000), 220 (94000) nm; cyclic voltammetry, $E_{p,oxi}$ 0.57, $E_{p,red}$ 0-44 V vs SCE.

Anal. Calcd. for $RuC_{34}H_{30}O_8S_2$: C, 55.80; H, 4.13. Found: C, 56.00; H, 4.09.

Bis(dimethyl sulfoxide)bis(4'-methoxyflavonato)ruthenium (II) (5):

This compound was obtained as a dark-brown powder, mp 210-211°; uv-vis: λ max (ε) 410 (81000), 316 (249000), 255 (sh, 195000), 223 (222000) nm; cyclic voltammetry, $E_{p,oxi}$ 0.53, $E_{p,red}$ 0.41V vs SCE.

Anal. Calcd. for $RuC_{36}H_{34}O_{10}S_2$: C, 54.61; H, 4.33. Found: C, 54.76; H, 4.24.

Bis(dimethyl sulfoxide)bis(3',4',5',7-tetramethoxyflavonato)ruthenium(II) (6):

This compound was obtained as a dark-brown powder, mp 189-190°; uv-vis: λ max (ε) 410 (20000), 322 (62000), 213 (125000) nm; cyclic voltammetry, $E_{p,oxi}$ 0-55, $E_{p,red}$ 0.42 V vs SCE.

Anal. Calcd. for $RuC_{42}H_{46}O_{16}S_2$: C, 51.88; H, 4.77. Found: C, 51.81; H, 4.65.

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