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Syntheses of 5-Hydroxyflavone-Transition Metal Complexes

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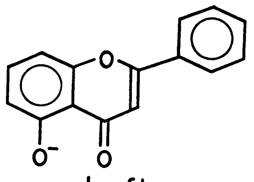
Synopsis. New complexes [M(hofl)$_2$(OH$_2$)$_n$] (Hhofl=5-hydroxyflavone; M=Co and Ni, n=2; M=Cu, n=1 and 0) and [M(hofl)$_3$] (M=V and Fe) were synthesized and characterized by IR and electronic absorption spectroscopy. Polynuclear ethoxo(5-hydroxyflavonato)metal(II) complexes of cobalt and copper were also prepared.

Many hydroxyflavone derivatives are distributed widely in plants.[1,2] Morin and quercetin have been used as reagents for colorimetric and fluorescent analyses of metals.[3] The analyses are based on the chelating ability of the hydroxyflavones with metals.[4–7] However, hardly any work has been reported as regards isolation and characterization of the hydroxyflavone–metal complexes.



hofl

This note deals with the syntheses and properties of some new transition metal complexes with 5-hydroxyflavone (Hhofl), one of the simplest model compounds of hydroxyflavones.

Experimental

Materials. 5-Hydroxyflavone was synthesized from 2,6-dihydroxyacetophenone according to the method of Looker *et al.*,[8] and identified by elemental analysis, melting point and IR spectrum. Commercial metal chlorides were used without further purification. Solvents were dried by the usual methods and distilled.

General Procedure. IR and electronic spectra were measured on Hitachi 285 and 323 spectrometers, respectively. Melting points were determined on a Yanagimoto MP-S3 microstage apparatus in capillary tubes and are uncorrected.

Preparation of Bis- or Tris(5-hydroxyflavonato)metal Complexes. 5-Hydroxyflavone (8.0 mmol) and nickel(II) chloride (3.0 mmol) were mixed in ethanol. An ethanol solution of sodium acetate (10.0 mmol) was added to the mixture with stirring. After the reaction mixture had been refluxed for 4 h, the resulting precipitate was separated, recrystallized from benzene–hexane and dried *in vacuo* to give a yellow solid, [Ni(hofl)$_2$(OH$_2$)$_2$] (yield 32%).

The complexes [Co(hofl)$_2$(OH$_2$)$_2$], [Cu(hofl)$_2$OH$_2$], and [Cu(hofl)$_2$] were prepared similarly. Tris(5-hydroxyflavonato)metal(III) complexes of vanadium and iron were also prepared in a similar way except that anhydrous metal(III) chloride was used in place of divalent metal chloride.

Preparation of Ethoxo(5-hydroxyflavonato)metal(II) Complexes. An ethanol solution containing 5-hydroxyflavone (4.2 mmol) and sodium ethoxide (2.0 mmol) was added gradually to an ethanol solution of cobalt(II) chloride (2.0 mmol). The reaction mixture was refluxed for 3 h. The resulting precipitate was collected and washed with benzene and ethanol to afford a reddish brown solid, [{Co(OEt)(hofl)}$_n$] (yield 63%). The complex, [{Cu(OEt)(hofl)}$_n$] was prepared in a similar way.

Results and Discussion

The yields, properties, and the results of elemental analyses of the complexes are summarized in Table 1. Diaquabis(5-hydroxyflavonato)metal(II) and the tris(5-hydroxyflavonato)metal(III) complexes are soluble in usual organic solvents such as benzene and chloroform but not in hexane. The water content of the mononuclear copper(II) complexes changes with the heating temperature in the drying procedure. [Cu(hofl)$_2$OH$_2$] and [Cu(hofl)$_2$] were obtained by drying *in vacuo* at 125—135 °C for 2 h and at 150—160 °C for 5 h, respectively. No diaqua complex of copper(II) was obtained in a pure state.

The spectroscopic data are summarized in Table 2. IR spectra of the 5-hydroxyflavonato complexes show

TABLE 1. YIELDS AND SOME PROPERTIES OF THE 5-HYDROXYFLAVONE–TRANSITION METAL COMPLEXES

Complex	Yield[a] (%)	Color	Mp (°C)	Elemental analyses[b] (%)		
				C	H	M
[Co(hofl)$_2$(OH$_2$)$_2$]	14	Orange yellow	233—237(dec)	63.51(63.27)	3.39(3.90)	—
[Ni(hofl)$_2$(OH$_2$)$_2$]	32	Yellow	298—299(dec)	63.42(63.30)	3.23(3.90)	10.19(10.32)[c]
[Cu(hofl)$_2$OH$_2$]	28	Olive yellow	274—280(dec)	64.82(64.80)	3.12(3.63)	—
[Cu(hofl)$_2$]	65	Olive yellow	>300	66.97(66.71)	3.29(3.38)	—
[V(hofl)$_3$]	21	Dark green	166.5—171.5	70.63(70.87)	3.76(3.57)	—
[Fe(hofl)$_3$]	33	Reddish violet	>300	70.76(70.41)	3.45(3.55)	—
[Co(OEt)(hofl)]	63	Reddish brown	>300	59.42(59.84)	3.11(4.18)	—
[Cu(OEt)(hofl)]	22	Yellow brown	>300	58.22(59.04)	3.00(4.08)	—

a) Calculated on the basis of metal chloride. b) Calculated values in parentheses. c) By gravimetric analysis of bis(dimethylglyoximato)nickel(II) derived from the sample.

Table 2. Spectroscopic data of 5-hydroxyflavone and its transition metal complexes

Compound	IR spectrum[a] ν(C=O) (cm^{-1})	Electronic spectrum[b]	
		ν_{max} (cm^{-1})	ε_{max}
Hhofl	1653	29800	4600
[Co(hofl)$_2$(OH$_2$)$_2$]	1639	24200	4400
[Ni(hofl)$_2$(OH$_2$)$_2$]	1639	24700	5800
[Cu(hofl)$_2$OH$_2$]	1627	—	—
[Cu(hofl)$_2$]	1618	24100	970
[V(hofl)$_3$]	1622	17800	1370
[Fe(hofl)$_3$]	1620	23500[c]	11600
[Co(OEt)(hofl)]	1635	—	—
[Cu(OEt)(hofl)]	1639	—	—

a) In KBr disk. b) In chloroform. c) Having a shoulder at 19230 cm^{-1}.

ν(CO) bands, shifting towards a frequency lower by 14—35 cm^{-1} from that observed for free 5-hydroxyflavone, indicating that the 5-hydroxyflavonato ligand is coordinated to the metal ion as a bidentate chelate. Both [Co(hofl)$_2$(OH$_2$)$_2$] and [Ni(hofl)$_2$(OH$_2$)$_2$] are assigned to a tetragonal bipyramid structure in consideration of its composition, by analogy with diaquabis(salicylaldehydato)nickel(II) complex.[9] [V(hofl)$_3$] and [Fe(hofl)$_3$] are ascribed to pseudo-octahedral structures.

The mononuclear complexes of iron(III), cobalt(II), nickel(II), and copper(II) exhibit a strong electronic absorption band near 24000 cm^{-1}, virtually independent of the metal ion. The intensity of this band is too strong to be assigned to a d-d transition. The band is located at a wave number lower by *ca.* 5800 cm^{-1} than the minimum energy absorption band of free 5-hydroxyflavone. Each of the iron(III), cobalt(II), nickel(II), and copper(II) ions in a ground state has one or more unoccupied d-orbitals. This indicates that the absorption band near 24000 cm^{-1} is ascribed to a charge transfer from the 5-hydroxyflavonato ligand to the metal d-orbital.

On the other hand, [V(hofl)$_3$] shows a strong absorption band at 17800 cm^{-1}, besides a very strong band above 21000 cm^{-1}. The intensity of these bands is so strong that it is unlikely that they are associated with the d-d transitions. The vanadium(III) ion with a d^2 configuration has a vacant d-orbital located at a lower energy level than the unoccupied d-orbitals of the nickel(II) and copper(II) ions. The band at 17800 cm^{-1} is assigned to a charge transfer from the 5-hydroxyflavonato ligand to the vacant low-lying d-orbital of the vanadium(III) ion, probably obscuring a low intensity band expected to appear at a similar wave number, owing to the d-d transition.[10]

The electronic spectra and the molecular weights of the ethoxo(5-hydroxyflavonato)metal(II) complexes could not be measured, because of the high insolubility in the usual organic solvents. These complexes are supposed to have polymeric structures, by analogy with alkoxo(salicylaldehydato)copper(II) and its related complexes.[11] Attempts to prepare ethoxo(5-hydroxyflavonato)nickel(II) were unsuccessful.

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