

Synthesis and Characterisation of Cobalt(II) Complexes of 3-Hydroxyflavone

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ABSTRAK

Sintesis diakuabis(3-hidroksiflavanato)kobalt(II) dan bis(piridina)bis(3-hidroksiflavanato)kobalt(II) dilaporkan. Hasil spektrum inframerah menunjukkan yang ligan 3-hidroksiflavanato membentuk kelat dengan kobalt(II) melalui kumpulan 3-hidroksi dan 4-keto. Spektrum elektronik kedua-dua kompleks pula memberi gambaran yang kobalt(II) membentuk kompleks oktahedron. Analisis kuantitatif kompleks yang diasingkan memberi padanan yang baik dengan nilai jangkaan. Pengukuran momen magnet menunjukkan yang kedua-dua kompleks adalah kompleks kobalt(II), d^7 berspin tinggi. Corak beraluan serbuk sinar-X bagi aduk piridina hampir meberi padanan 1:1 dengan corak belauan serbuk sinar-X bagi *trans*-bis(piridina)bis(3-hidroksiflavanato)nikel(II) yang mempunyai geometri oktahedron. Dengan demikian boleh disimpulkan yang bis(piridina)bis(3-hidroksiflavanato)kobalt(II) juga berkoordinat secara oktahedron dengan dua anion 3-hidroksiflavanato membentuk kelat dan dua molekul piridina berada dalam kedudukan *trans*.

ABSTRACT

The syntheses of diaquabis(3-hydroxyflavanato)cobalt(II) and bis(pyridine)bis(3-hydroxyflavanato)cobalt(II) are described. Results from infrared spectra clearly show that the 3-hydroxyflavanato anion forms a chelate through the 3-hydroxy 4-keto groups. The electronic spectra of both complexes indicate that cobalt(II) has an octahedral geometry. Quantitative analyses of the isolated products gave good agreement with calculated values. Magnetic moment measurements show that both compounds are high spin d^7 cobalt(II) complexes. The powder diffraction pattern of the pyridine adduct gave almost 1:1 correspondence with *trans*-bis(pyridine)bis(3-hydroxyflavanato)nickel(II) which has an octahedral geometry. Therefore, it is highly likely that bis(pyridine)bis(3-hydroxyflavanato)cobalt(II) is octahedrally co-ordinated with two chelating 3-hydroxyflavanato anions and two pyridine molecules occupying *trans* positions.

Keywords: cobalt(II) complex, 3-hydroxyflavanato

INTRODUCTION

Flavonoids belong to a large group of compounds which occur naturally in plants (Harborne *et al.* 1975). Flavonoids have a basic skeleton structure as shown in *Fig. 1*. Ring B may be either saturated or unsaturated. Flavonoids with an unsaturated B ring and a keto group in the 4 position are called flavones. Flavones with a hydroxyl group in the 3 position are collectively known as flavonols. Flavonols with hydroxy groups in other positions are found in practically all plants (Herrmann 1976). For example, quercetin and kaempferol occur in the skin of apples and pears (Herrmann 1976). Cobalt can also be found in a variety of plants, but the exact mechanism by which cobalt is taken up by plants is not thoroughly understood (Fargo 1981). However, it is likely that cobalt forms a complex when it gets into the plant system (Skaar *et al.* 1973). Since flavonols are widespread in plants it is possible that cobalt could form complexes with this class of compounds.

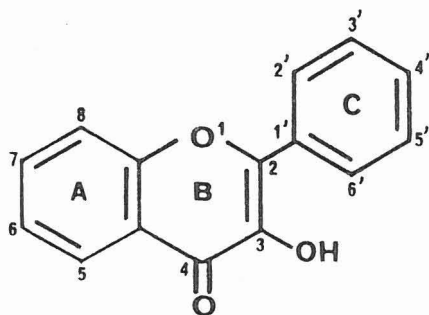


Fig. 1

Complex formation between 3-hydroxyflavone and aluminium(III) chloride was studied spectrometrically by Jurd and Geissman (1956). Like many other flavonols, the complexing capability of 3-hydroxyflavone is also demonstrated by its wide use as an analytical reagent. The reagent 3-hydroxyflavone has been used for the fluorimetric determination of metals (Katyal and Prakash 1977; Cabrera-Martin *et al.* 1986). To date, the only complexes of 3-hydroxyflavone that have been isolated are a series of air-stable organotin derivatives (Blunden and Smith 1982) and chelates with copper(I) (Speier *et al.* 1990) and copper(II) (Balogh-Hergovich *et al.* 1991). The crystal structure of *trans*-bis(pyridine)bis(3-hydroxyflavonate)nickel(II) has been elucidated (Yang Farina *et al.* 1995). Nickel(II) is hexacoordinated and the geometry surrounding the metal centre is close to an octahedron. The metal centre is bound to two chelating bidentate 3-hydroxyflavonate anions and two pyridine molecules which occupy *trans* positions.

Since all flavonols contain the 3-hydroxy-4-keto group, it was thus logical to study the complex formation capability of this site. We therefore decided to look at the complex formation between cobalt(II) and 3-hydroxyflavone by synthesizing and characterizing such complexes.

MATERIALS AND METHODS

Commercial grade 3-hydroxyflavone (flvH) and analar grade cobalt(II) chloride hexahydrate were supplied by Aldrich Chemicals and Fisons respectively. Commercial grade triethylamine (Et_3N) and pyridine (py) were purchased from BDH and used without further purification.

Elemental C, H, and N analyses were made on an F and M scientific 185C analyser at the University of Reading, England. The quantitative determinations for cobalt were obtained using a Perkin-Elmer 272 atomic absorption spectrophotometer at $\lambda = 240.7 \text{ nm}$. The infrared spectra were recorded from mulls in hexachlorobut-1,3-diene ($4000\text{-}2500$ and $1600\text{-}1200 \text{ cm}^{-1}$) and nujol ($2500\text{-}1600$ and $1200\text{-}400 \text{ cm}^{-1}$ between KBr plates using a Perkin-Elmer 983 grating spectrophotometer. The magnetic moment of the complexes was calculated at room temperature on a Faraday balance using $\text{Hg}[\text{Co}(\text{NCS})_4]_2$ ($\chi_g = 16.44 \times 10^{-6} \text{ cgs units}$) as calibrant. The diffuse reflectance spectra of solid samples were measured from $50000\text{-}5000 \text{ cm}^{-1}$ on a Beckman Acta MIV spectrophotometer. The X-ray powder patterns were determined on a Philips X-ray diffractometer (PW30/1320) using filtered Co-K ∞ radiation ($\lambda = 1.7902 \text{ \AA}$).

All preparations were carried out under an atmosphere of nitrogen using thoroughly deoxygenated solutions.

SYNTHESIS OF DIAQUABI

(3-HYDROXYFLAVONATO)COBALT(II)

$[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$ Cobalt(II) chloride (0.2 g, 1 mmol) was dissolved in ethanol (20 ml). This mixture was added to a lemon-yellow ethanolic solution of 3-hydroxyflavone (0.5 g, 2 mmol) and triethylamine (0.3 ml, 2 mmol). Initially the mixture turned brown, but on further stirring a brown precipitate was formed. The resulting mixture was then subjected to heating under reflux (79°C) for 30 minutes. Upon cooling the brown solid was isolated by filtration, washed with ethanol ($2 \times 5 \text{ ml}$) and dried in a vacuum desiccator over phosphorous pentoxide, yield = 0.5 g (88%).

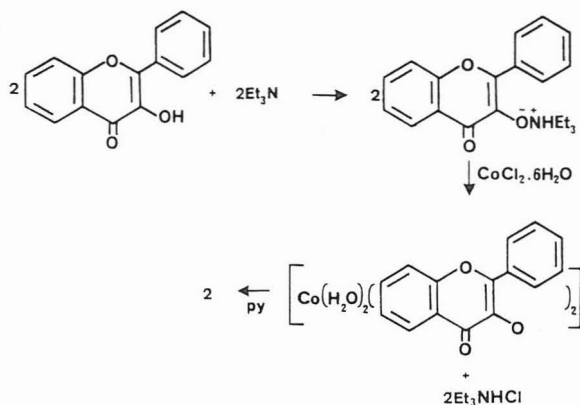
SYNTHESIS OF BIS(PYRIDINE)BIS

(3-HYDROXYFLAVONATO)COBALT(II)

$[\text{Co}(\text{py})_2(\text{flv})_2]$ This complex was prepared by heating under reflux (116°C) a mixture of $[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$ and excess pyridine. Upon cooling brown crystals were deposited. Recrystallization from hot acetonitrile afforded brown single crystals.

RESULTS AND DISCUSSION

Elemental analyses for both complexes are presented in Table 1. The data showed good agreement with proposed formulae. The addition of triethylamine to 3-hydroxyflavone resulted in the abstraction of the acidic proton to give the triethylammonium salt of 3-hydroxyflavone as the intermediate. Addition of cobalt(II) chloride hexahydrate gave the bis chelate with two water molecules still attached to the metal centre. A side product in this reaction is triethylammonium chloride which is soluble in ethanol. Hence simple filtration and washing with ethanol gave diaquabis(3-hydroxyflavonato)cobalt(II). The complex $[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$ gave negative results when tested for the presence of chloride ions. A reaction involving a stoichiometric ratio of 3:1, hydroxyflavonato anion : cobalt(II) was carried out in an attempt to prepare $[\text{Et}_3\text{NH}][\text{Co}(\text{flv})_3]$. However the product isolated gave identical results to those of $[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$. The reaction between $[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$ and pyridine gave the substitution product $[\text{Co}(\text{py})_2(\text{flv})_2]$ which was easily purified by recrystallization from hot acetonitrile. A simple outline of the reaction mechanism is given in Scheme 1.



Scheme 1. Reaction layout

The infrared spectra of the complexes were compared to those of the free ligand. The infrared data of $[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$ and $[\text{Co}(\text{py})_2(\text{flv})_2]$ are presented in Table 2. Generally, upon complex formation, major changes occurred in the 4000-3000 and 1650-1500 cm^{-1} regions. The infrared spectrum of the free ligand showed that $\nu(\text{O-H})$ appeared as a strong broad peak at 3215 cm^{-1} . As expected, this peak disappeared when the ligand formed complexes with cobalt(II). However, the presence of water

TABLE 1
Analytical results for cobalt(II) 3-hydroxyflavonato complexes

Compound	%C	%H	%N	%Co
[Co(H ₂ O) ₂ (flv) ₂]	63.93 (63.28)	3.73 (3.89)	- -	10.40 (10.35)
[Co(py) ₂ (flv) ₂]	69.60 (69.47)	4.21 (4.08)	4.16 (4.05)	8.00 (8.52)

Calculated values are given in parentheses.

in [Co(H₂O)₂(flv)₂] was detected by a broad peak due to $\nu(\text{O-H})$ at 3450 cm^{-1} and a weak $\delta(\text{O-H})$ at 1682 cm^{-1} . The C=C ring stretching vibrations of the free ligand occur at 1627, 1611 and 1563 cm^{-1} , while $\nu(\text{C=O})$ is superimposed upon the peak at 1611 cm^{-1} (Jose *et al.* 1974). Complex formation in both compounds is clearly shown by shifts in $\nu(\text{C=C})$ and $\nu(\text{C=O})$ vibrations. The ring stretching vibrations appeared at 1613, 1591 and 1570 cm^{-1} in 1 while in [Co(py)₂(flv)₂] the peaks are located at 1614, 1590 and 1568 cm^{-1} . The intensity of the peaks at 1613 and 1614 cm^{-1} is weaker than the same peak in the free ligand since the carbonyl stretching wavenumber is now lowered to 1545 and 1547 cm^{-1} in [Co(H₂O)₂(flv)₂] and [Co(py)₂(flv)₂] respectively. The lowering of the carbonyl stretch indicates that the strength of the C=O bond is weakened because the oxygen atom is also bonded to cobalt(II), thus reducing the electron density between oxygen and carbon. This observation is in accordance with those reported by other workers (Jose *et al.* 1974; Blunden and Smith 1982). The lowering of the carbonyl stretch coupled with the absence of $\nu(\text{O-H})$ clearly indicates that the cobalt(II) anion is attached to both 4-keto and 3-hydroxy groups. Therefore it can be induced that the 3-hydroxyflavonato anion forms a chelate with cobalt(II). The infrared spectrum of [Co(py)₂(flv)₂] contains additional peaks of medium intensities centred at 748 and 702 cm^{-1} which were assigned to pyridine, C-H out of plane deformation bands.

The magnetic moments of [Co(H₂O)₂(flv)₂] and [Co(py)₂(flv)₂] at 293 K were measured to be 4.67 and 4.98 BM respectively and are comparable to the magnetic moment of other high spin d^7 octahedral complexes such as [Co(H₂O)₂(sal)₂] (sal=salicylaldehydato anion), which has a value of 4.74 BM (Cotton and Holm 1960). Octahedral cobalt(III) complexes on the other hand, being d^6 are usually low spin because of the inert t_{2g}^6 configuration. However, the hexafluorocobaltate anionic complex, [CoF₆]³⁻ is paramagnetic and has a magnetic moment of about 5.4 BM. Therefore it can be concluded that both complexes are high spin cobalt(II) complexes since a high spin cobalt(III) complex should give a much higher magnetic moment.

TABLE 2
Infrared data of $[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$ and $[\text{Co}(\text{py})_2(\text{flv})_2]$

$[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$	$[\text{Co}(\text{py})_2(\text{flv})_2]$		
	(cm ⁻¹)		
3423(b,m)	998(w)	3087(w)	995(w)
3095(w)	924(w)	3069(m)	945(w)
1682(b, w)	910(m)	3034(w)	918(w)
1613(m)	769(m)	1614(m)	908(m)
1519(s)	755(s)	1590(s)	768(m)
1570(m)	719(w)	1568(s)	757(m)
1545(vs)	712(w)	1547(vs)	748(s)
1505(s)	688(m)	1515(s)	717(w)
1487(vs)	676(m)	1483(s)	702(sh, m)
1461(s)	664(m)	1465(sh, s)	688(m)
1440(m)	537(w)	1442(sh, s)	662(m)
1420(vs)	485(w)	1413(vs)	529(w)
1359(m)		1358(m)	486(m)
1325(m)		1321(s)	
1313(m)		1312(m)	
1299(m)		1297(m)	
1253(m)		1253(m)	
1220(sh, s)		1215(sh,vs)	
1185(w)		1180(m)	
1154(s)		1150(s)	
1118(m)		1114(m)	
1076(w)		1099(m)	
1035(w)		1072(m)	
1027(w)		1059(m)	
1004(w)		1035(m)	
		1005(m)	

vs = very strong; s = strong; m = medium; w = weak;
sh = shoulder; b = broad.

The reflectance spectrum of 3-hydroxyflavone contained two peaks at 7300 and 9000 cm⁻¹ which are due to the third $\nu(\text{C-H})$ overtone band. Hence when examining the electronic spectra of these 3-hydroxyflavonato complexes, bands which should appear in the region 6000-10000 cm⁻¹ cannot be accurately assigned as these bands will overlap with the absorption caused by the C-H overtone band. In the spectra of these complexes, peaks which appear above 20000 cm⁻¹ are the result of charge transfer processes, which are strong in intensity, thereby engulfing the peaks due to electronic transition. In the electronic spectra of high spin cobalt(II)

octahedral complexes, the ${}^4A_{2g}$ level is usually close to the ${}^4T_{1g}(P)$ level, hence the transitions from the lower ${}^4T_{1g}(F)$ level to these two upper levels are close together. For example, in the complex $[\text{Co}(\text{dmsO})_6]^{2+}$ (dmsO = dimethyl sulphoxide) there were two peaks at 14600 and 18700 cm^{-1} corresponding to the transitions described above (Elder 1968). The peaks observed in the 10000-20000 cm^{-1} region are given the appropriate assignments as shown in Table 3. In the reflectance spectrum of $[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$ there were two peaks at 14300 and 17400 cm^{-1} which can be ascribed to the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions respectively. In the analogous pyridine adduct, these transitions appeared at 14300 and 17500 cm^{-1} . These transitions are comparable to those reported for $[\text{Co}(\text{dmsO})_6]^{2+}$ and therefore it is likely that $[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$ and $[\text{Co}(\text{py})_2(\text{flv})_2]$ are octahedral complexes.

TABLE 3
Electronic transitions of $[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$ and
 $[\text{Co}(\text{py})_2(\text{flv})_2]$ observed between 10000-20000 cm^{-1}

Compound	Wavenumber(cm^{-1})	Assignments
$[\text{Co}(\text{H}_2\text{O})_2(\text{flv})_2]$	14300	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$
	17400	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$[\text{Co}(\text{py})_2(\text{flv})_2]$	14300	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$
	17500	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$

The d -spacings for $[\text{Co}(\text{py})_2(\text{flv})_2]$ and the analogous nickel(II) complex, $[\text{Ni}(\text{py})_2(\text{flv})_2]$ are given in Table 4. Comparison between the two sets of data clearly show that $[\text{Co}(\text{py})_2(\text{flv})_2]$ is isomorphous with the nickel complex because the d -spacings gave almost 1:1 correspondence. Therefore, it can be concluded that the cobalt complexes have the same structure as the nickel complex. This is not surprising since many cobalt(II) complexes have been found to be isostructural with the analogous nickel(II) compounds (Hashagen and Fackler 1965; Buchanan *et al.* 1979). This feature is due to the equality of the ionic radii of cobalt(II) and nickel(II) which is 0.78 Å for both metal ions.

CONCLUSION

The reaction between the 3-hydroxyflavonato anion and cobalt(II) chloride hexahydrate gave rise to diaquabis(3-hydroxyflavonato) cobalt(II). Treat-

TABLE 4
d-Spacings for [Co(py)₂(flv)₂] dan [Ni(py)₂(flv)₂]

[Co(py) ₂ (flv) ₂]		[Ni(py) ₂ (flv) ₂]	
<i>d</i> Å	I	<i>d</i> Å	I
9.17	vs	9.17	vs
7.61	w	7.72	w
7.09	w	7.24	w
5.59	w	5.64	w
5.36	m	5.39	w
4.93	w	4.95	m
4.80	m	4.79	w
4.32	w	4.30	w
4.07	m	4.08	m
3.92	m	3.96	m
3.83	w	3.81	w
3.68	w	3.68	w
3.50	w	3.54	w
3.35	w	3.38	w

ment of the water adduct with pyridine gave bis(pyridine)bis(3-hydroxyflavonato)cobalt(II). In both complexes the anion is chelated to the metal ion through the 3-hydroxy and 4-keto groupings as demonstrated by the infrared spectra. Results of diffuse reflectance spectra indicate that both complexes are octahedral in nature and magnetic moment measurements show that they are cobalt(II) complexes with a high spin *d*⁷ configuration. Results of X-ray powder diffraction studies imply that bis(pyridine)bis(3-hydroxyflavonato)cobalt(II) has the same structure as the corresponding nickel(II) complex. Therefore we can deduce that the geometry surrounding the cobalt(II) ion in [Co(py)₂(flv)₂] is an octahedron and the pyridine molecules like the nickel complex also occupy *trans* positions.

REFERENCES

- BALOGH-HERGOVICH, E., G. SPEIER and G. ARGAY. The oxygenation of copper(I) and copper (II) flavonolate complexes. The crystal structure and molecular structure of bis(flavonolato)copper(II). *J. Chem. Soc. Chem. Commun.* 551-552.
- BLUNDEN, S.J. and J.P. SMITH. 1982. Synthesis and spectroscopic studies of organotin derivatives of 3-hydroxyflavone. *J. Organomet. Chem.* **226**: 157-163.
- BUCHANAN, R.M., B.J. FITZGERALD and C.G. PIERPONT. 1979. Semiquinone radical anion coordination to divalent cobalt and nickel. Structural features of the bis(3,5-di-*tert*-1,2-semiquinone)cobalt(II) tetramer. *Inorg. Chem.* **18**: 3439-3444.

- CABRERA-MARTIN, A., J.S. DURAND and S. RUBIO-BARROSO. 1986. Fluorometric determination of chromium at low levels with 3-hydroxyflavone and determination of chromium at low levels with 3-hydroxyflavone and application of the method to steels. *Anal. Chim. Acta* **183**: 263-267.
- COTTON, F.A and R.H. HOLM. 1960. Magnetic investigations of spin-free cobaltous complexes. III. On the existence of planar complexes. *J. Am. Chem. Soc.* **82**: 2979-2983.
- ELDER, R.C. 1968. Base adducts of bis(2,4-pentanedionato)cobalt(II). The crystal and molecular structure of *trans*-bis(2,4-pentanedionato)dipyridine cobalt(II), Co(AA)₂(py)₂. *Inorg. Chem.* **7**: 1117-1123.
- FARAGO, M.E. 1981. Metal tolerant plants. *Coord. Chem. Rev.* **36**: 155-182.
- HARBONE, J.B., T.J. MABRY and H. MABRY. 1975. *The Flavonoids*. London: Chapman and Hall,
- HASHAGEN, J.T. and J.P. FACKLER, Jr. 1965. Base adducts of β-ketoenolates. III. Complexes of cobalt(II). *J. Am. Chem. Soc.* **87**: 2821-2824.
- HERRMANN, K. 1976. Flavonols and flavones in food plants: a review. *J. Food Technol.* **24**: 433-448.
- JOSE, C.I., P.S. PHADKE and A.V. RAMA RAO. 1974. Infrared spectra of flavones and isoflavones: effect of iodine and boron trifluoride on carbonyl frequencies. *Spec. Chim. Acta* **30A**: 1199-1206.
- JURD, L. and T.A. GEISSMAN. 1956. Absorption spectra of metal complexes of flavonoid compounds. *J. Organomet. Chem.* **21**: 1395-1401.
- KATYAL, M. and S. PRAKASH. 1977. Analytical reactions of hydroxyflavones. *Talanta* **24**: 367-375.
- SKAAR, H., E. OPHUS and B.M. GULLVAG. 1973. Lead accumulation within nuclei of moss leaf cells. *Nature (London)*. **241**: 215-216.
- SPEIER, G., E. FÜLÖP and L. PARKANYI. 1990. Chelated flavonol co-ordination in flavonolatobis(triphenylphosphine)copper(I). *J. Chem. Soc. Chem. Commun.* 512-513.
- YANG FARINA, BOHARI M. YAMIN, HOONG-KUN FUN, BOON-CHUAN YIP and SIANG-GUAN TEOH. 1995. *trans*-[Bis(3-hydroxy-2-phenyl-4H-benzopyran-4-onato)bis(pyridine) nickel(II)] *Acta Cryst.* **C51** [in press].