

## Derivatives of 1,3-Bis-(2-hydroxyphenyl)-1,3-propanedione. An Attempt to Get More Soluble Heterotrinnuclear Complexes. Crystal Structure of Chromium Tris-(1,3-bis-(2-hydroxyphenyl)-1,3-propanedionate)

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### Abstract

The substitution of a hydrogen atom by other radicals has been achieved in 1,3-bis-(2-hydroxyphenyl)-1,3-propanedione (bhppH<sub>3</sub>) at the methinic carbon by reacting the Co(II) complex of this  $\beta$ -diketone with different electrophiles. In most of the cases the reaction proceeded further to yield the corresponding flavones. To have a better range of solvents to carry on these reactions the Fe<sup>3+</sup> and Cr<sup>3+</sup>-bhppH<sub>3</sub> complexes were synthesized. The TLC of the solids obtained indicated the existence of several M-bhppH<sub>3</sub> complexes. The crystal structure of the Cr(bhppH<sub>2</sub>)<sub>3</sub>·0.5toluene is reported. Triclinic,  $P\bar{1}$ ,  $a = 14.282(3)$ ,  $b = 14.127(3)$ ,  $c = 12.240(2)$  Å,  $\alpha = 123.24(3)$ ,  $\beta = 94.72(2)$ ,  $\gamma = 90.87(2)^\circ$ ,  $V = 2053(1)$  Å<sup>3</sup>,  $Z = 2$ . Reaction of Fe(bhppH<sub>2</sub>)<sub>3</sub> with NBS yielded, after working up with SCN<sup>-</sup>, mostly dibrominated derivatives. Reaction of 2-diphenylmethyl-1,3-(2-hydroxyphenyl)-1,3-propanedione (dpmbhppH<sub>3</sub>) with M(AcO)<sub>2</sub>·xH<sub>2</sub>O in pyridine (M = Ni, Co) yielded M<sub>3</sub>(dpmbhpp)<sub>2</sub>·6py. The introduction of the R group at the methinic carbon lowers its reactivity.

### Introduction

The area of polynuclear metal complexes has seen extensive growth, stimulated by interest in fields such as metalloenzymes, homogeneous catalysis, electrical conductance and magnetic exchange processes. The literature in this area is exhaustive [1], mainly dealing with dimeric compounds. On the contrary little has been done with linear trinuclear compounds and particularly less with heterotrinnuclear complexes [2, 3].

Trinuclear linear metal complexes with metal distributions (UO<sub>2</sub>)M(UO<sub>2</sub>) (M = Zn, Cu, Ni, Co, Fe, Mn) have already been obtained by Lindvedt and coworkers [2] by using the ligand 1,7-diphenyl 1,3,5,7-heptanetetrono, and the crystal and molecular structure of some of them have been reported, however to date no such simple heterotrinnuclear compounds with only transition metal ions have been described.

With the aim of obtaining this last type of compound, we have been working with 1,3-bis-(2-hydroxyphenyl)-1,3-propanedione (bhppH<sub>3</sub>), a ligand with two different types of reacting sites; one more reactive and placed in the central part (the  $\beta$ -diketone moiety) and two less reactive and placed outerly (the ketophenol moieties). Isomerically pure mononuclear complexes M(bhppH<sub>2</sub>)<sub>2</sub> with divalent transition or main group metals can therefore be obtained [4–8]. Both bhppH<sub>2</sub> moieties are placed in the same plane, and the metal is bonded to each one via the  $\beta$ -diketone functionality. This permits the use of these mononuclear complexes as ligands towards M' ions and trinuclear linear complexes which can be represented as MM'M or M'MM' can be obtained. One of the problems we have found so far is the high insolubility of these compounds, which has precluded the growth of crystals, and consequently the opportunity to confirm unambiguously the proposed structure. To solve this problem we planned to introduce substituents on the bhppH<sub>3</sub> methinic carbon, which would enhance the solubility of the resulting trinuclear complexes. The present paper concentrates on the synthesis of bhppH<sub>3</sub> related ligands, their complexes, and the facile dehydration reaction encountered in these compounds to yield the corresponding flavones. In particular the crystal and molecular structure of Cr(bhppH<sub>2</sub>)<sub>3</sub>, the synthesis and characterization of homotrinnuclear complexes CoCoCo and NiNiNi

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with 2-diphenyl-methyl-1,3-bis-(2-hydroxyphenyl)-1,3-propanedione (dpmbhppH<sub>3</sub>), as well as a new method to get free the organic moieties in these complexes is described. This last reaction could be particularly appropriate in the case of  $\beta$ -diketones acid or base sensitives.

## Experimental

### Starting Materials

All reagents and solvents were commercial grade materials and were used without further purification. Co(bhppH<sub>2</sub>)<sub>2</sub>·2CH<sub>3</sub>OH [5] and tris-(3-bromo-2,4-pentanedionate)iron(III) [9] were synthesized by previously described methods.

### Synthesis of 2-Diphenylmethyl-1,3-bis-(2-hydroxyphenyl)-1,3-propanedione (dpmbhppH<sub>3</sub>) (III)

To a solution of Co(bhppH<sub>2</sub>)<sub>2</sub>·2CH<sub>3</sub>OH (1.58 mmol, 1.0 g) in thf (75 ml) was added, with stirring, bromodiphenylmethane (3.16 mmol, 0.78 g) in thf (20 ml), and a small amount of CoBr<sub>2</sub>·6H<sub>2</sub>O in 1–2 ml of thf. The mixture was refluxed for 3 h and then was allowed to cool to room temperature (r.t.). During this time the color of the solution turned from reddish to greenish. The solution was evaporated and the residue extracted with water/ether. The suspended solid (2'-hydroxyflavone) in between both phases was discarded. The ethereal layer was dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to yield an oil. This was dissolved in hot methanol, and on cooling an off-white solid was obtained. Yield 56%. *Anal.* Found: C, 79.53; H, 5.04. Calc. for C<sub>28</sub>H<sub>22</sub>O<sub>4</sub>: C, 79.62; H, 5.21%.

### Synthesis of 3-Diphenylmethyl-2'-hydroxyflavone (V)

To a solution of dpmbhppH<sub>3</sub> (0.47 mmol, 0.2 g) in hot methanol (20 ml) was added NaMeO in methanol (1.42 mmol,  $\approx$ 4 ml), and Zn(AcO)<sub>2</sub>·2H<sub>2</sub>O (0.71 mmol, 0.156 g), in this order. The resulting mixture was refluxed for 10 min, and allowed to stand at r.t. for one week. A white solid precipitated, which was filtered and dried *in vacuo*. *Anal.* Found: C, 83.24; H, 4.80. Calc. for C<sub>28</sub>H<sub>20</sub>O<sub>3</sub>: C, 83.17; H, 4.95%.

### Synthesis of 3-(2-Nitrobenzenesulfenyl)-2'-hydroxyflavone (VI)

To a cold solution (0 °C) of Co(bhppH<sub>2</sub>)<sub>2</sub> (0.352 mmol, 0.2 g) in thf (20 ml) was added 2-nitrobenzenesulfenyl chloride (0.704 mmol, 0.133 g). The resulting solution was stirred and kept at 0 °C for 30 min. During this time the color of the solution turned from reddish to greenish. The working up procedure was analogous to that described for V. *Anal.* Found: C, 64.50; H, 3.32; N, 3.57. Calc. for C<sub>21</sub>H<sub>13</sub>O<sub>5</sub>NS: C, 64.45; H, 3.32; N, 3.51%.

### Synthesis of M<sub>3</sub>(dpmbhpp)<sub>2</sub>·6py (M = Ni, Co) (XI–XII)

To a warm solution of dpmbhppH<sub>3</sub> (0.474 mmol, 0.2 g) in methanol (20 ml) was added NaMeO (1.422 mmol) in methanol ( $\approx$ 4 ml) and after 10 min, M(AcO)<sub>2</sub>·4H<sub>2</sub>O (0.711 mmol, 0.18 g). The resulting mixture was refluxed for 15 min, and then was allowed to cool to r.t. During this time a solid begun to separate which was collected by filtration 24 h later, washed with methanol and dried *in vacuo*. This solid was treated with the minimum volume of pyridine able to dissolve it, discarding any insoluble material. The pyridinic solution was allowed to stand in an open vessel for 24 h yielding a crystalline solid which was separated, filtered and dried *in vacuo*. *Anal.* Found: C, 69.66; H 4.83; N, 5.36. Calc. for C<sub>86</sub>H<sub>68</sub>O<sub>8</sub>N<sub>6</sub>Ni<sub>3</sub>: C, 69.35; H, 4.57; N, 5.64%. Found: C, 69.29; H, 4.68; N, 5.81. Calc. for C<sub>86</sub>H<sub>68</sub>O<sub>8</sub>N<sub>6</sub>Co<sub>3</sub>: C, 69.35; H, 4.57; N, 5.64%.

### Synthesis of Cr(bhppH<sub>2</sub>)<sub>3</sub> (VII)

To a warm solution of bhppH<sub>3</sub> (1.56 mmol, 0.4 g) in isopropanol (40 ml) was added with stirring Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.65 mmol, 0.26 g) in the same solvent (20 ml). The resulting mixture was kept at 70 °C for 1 h. During this time the color of the solution turned from pale reddish to dark brown. After cooling at r.t. a dark brown crystalline solid precipitated which was collected by filtration, washed with water and dried *in vacuo* (yield 0.10 g).

The filtrate was chromatographed on silica gel (benzene) and after evaporation of the first dark fraction, an additional crop of crystals (0.07 g) was obtained. Recrystallization from hot toluene gave violet crystals. *Anal.* Found: C, 66.14; H 4.14. Calc. for C<sub>45</sub>H<sub>33</sub>CrO<sub>12</sub>: C, 66.10; H, 4.04%.

If instead of doing the chromatography the filtrate was kept in the fridge (4 °C) for 18 h an off-white solid was obtained (30 mg) which was identified as 3-nitro-2'-hydroxyflavone (VIII). *Anal.* Found: C, 63.34; H, 2.90; N, 5.07. Calc. for C<sub>15</sub>H<sub>9</sub>NO<sub>5</sub>: C, 63.60; H, 3.18; N, 4.95%. ME(EI) base peak at 283 m/e.

### Synthesis of Fe(bhppH<sub>2</sub>)<sub>3</sub>·2H<sub>2</sub>O (IX)

This compound was made following the procedure for Cr(bhppH<sub>2</sub>)<sub>3</sub>. No attempt was made to increase the yield by chromatography. *Anal.* Found: C, 63.20; H, 4.25. Calc. for C<sub>45</sub>H<sub>37</sub>FeO<sub>14</sub>: C, 63.02; H, 4.32%.

### Reaction of Fe(bhppH<sub>2</sub>)<sub>3</sub>·2H<sub>2</sub>O with NBS

A mixture of *N*-bromosuccinimide (0.67 g, 3.75 mmol) and Fe(bhppH<sub>2</sub>)<sub>3</sub> (0.77 g, 0.94 mmol) in 60 ml of chloroform was boiled for 10 min, washed with aqueous sodium bisulfite and then washed with water. A solid appeared in between both layers which was separated by filtration. This compound was

identified as 3-bromo-2'-hydroxyflavone (**X**). *Anal.* Found: C, 56.12; H, 2.72. Calc. for  $C_{15}H_9BrO_3$ : C, 56.78; H, 2.84%. ME(EI): 318(94%), 316(100%).

The resulting organic layer was treated with aqueous  $NH_4SCN$  (0.45 g, 50 ml) containing 1 drop of conc. HCl (3 times). The yellowish solution was dried with  $Na_2SO_4$ , evaporated and chromatographed with silica gel to yield several fractions, which were separated and analyzed either by ME or ME/elemental analysis. Among them was found dibromo-2'-hydroxyflavone (yield = 0.1 g). *Anal.* Found: C, 45.70; H, 2.45. Calc. for  $C_{15}H_8Br_2O_3$  ( $M = 396$ ): C, 45.45; H, 2.27%. ME(EI) 397(49.3%), 395(100%), 393(50.7%) *m/e*.

#### Reaction of Tris-(3-bromo-2,4-pentanedionate)-iron-(III) with NBS

The reaction and working up procedure is as indicated in the former case. The ME analysis of the first column chromatography fractions (chloroform) (75% yield) indicates the existence of at least two species: mono and dibrominated derivatives of acacH. ME(EI) monobrominated acacH 178(18%), 180(17%); dibrominated acacH 214(29%), 216(57%), 218(28%) *m/e*.

### Crystal Structure Determination

#### Crystal Data

Formula  $C_{45}H_{33}O_{12}Cr \cdot 0.5C_7H_8$ ,  $M_w = 860.8$ , triclinic,  $P\bar{1}$ ,  $a = 14.282(3)$ ,  $b = 14.127(3)$ ,  $c = 12.240(2)$  Å,  $\alpha = 123.24(3)$ ,  $\beta = 94.72(2)$ ,  $\gamma = 90.87(2)^\circ$ ,  $V = 2053(1)$  Å<sup>3</sup>,  $D_x = 1.39$  g cm<sup>-3</sup>,  $Z = 2$ ,  $F(000) = 896$ ,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu(Mo K\alpha) = 3.62$  cm<sup>-1</sup>. Room temperature.

#### Experimental

A (0.1 × 0.1 × 0.2 mm) crystal was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from 25 reflections ( $4 \leq \theta \leq 12^\circ$ ) and refined by least squares. Intensities were collected with graphite monochromatized Mo K $\alpha$  radiation, using the  $\omega$ -scan technique, (scan width 1°, scan speed 0.03° s<sup>-1</sup>). 4528 intensities were measured in the range  $2 \leq \theta \leq 25^\circ$ , 4473 of which were assumed as observed applying the condition  $I \geq 2.5\sigma(I)$ . Three reflections were measured every two hours as orientation and intensity control, significant intensity decay was not observed. Lorentz, polarization but not absorption corrections were made.

The Cr atom was located from a Patterson synthesis, the remaining non-hydrogen atoms from DIRDIF computer system [10]. The structure was isotropically and anisotropically refined by full-matrix least squares method, using the SHELX76 [11] computer program;  $f$ ,  $f'$  and  $f''$  were taken

from International Tables of X-ray Crystallography. The function minimized was  $\Sigma \omega ||F_o| - |F_c||^2$ , where  $\omega = (\sigma^2(F_o + 0.026|F_o|^2))^{-1}$ . A subsequent difference synthesis carried out after the three isotropic cycles shows a disorder in the localization of O(32) and several peaks which could be assigned to a toluene molecule. 26 H (of 47) atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and anisotropically the remaining atoms, occupancy factor of O(32) atom, were also refined obtaining a value of 0.80(2) for O(32) and 0.20 for O(32). The occupancy factor of 0.5 for the toluene molecule was assigned according to Fourier peaks height. The final  $R$  was 0.075 ( $R_w = 0.084$ ) for all observed reflections.

#### Description of the Structure

The structure consists of Cr ions linked to three O–C(C<sub>6</sub>H<sub>4</sub>OH)–CH–C(C<sub>6</sub>H<sub>4</sub>OH)–O ligands in the *cis*-position and displaying a distorted octahedral coordination. The average Cr–O bond distance is 1.951(8) Å. The Cr<sub>3</sub>O<sub>2</sub> six membered rings have a skew half chair form with Cr atom deviating 0.43(8) Å (average value) from the plane defined by the remaining five atoms. The average C=O and C–C bond lengths and O–Cr–O, C–O–Cr, O–C–C and C–C–C bond angles of these rings are 1.297(5), 1.402(12) Å, 88.9(2), 127.4(11), 122.7(5) and 124.8(8)°, respectively. The main differences in the crystal structure are due to packing forces and correspond to localization of phenyl rings, the torsion angles O(X)–C(X)–C(X1)–C(X2) are –16.7(2), –1.5(6), –166.8(6), –9.9(6), 3.6(6) and –6.1(6)° for  $X = 1, \dots, 6$  respectively. Fractional atomic coordinates are shown in Table I. Selected bond lengths and angles are indicated in Table II. A perspective view of the molecule is shown in Fig. 1.

### Results and Discussion

The substitution of a hydrogen atom by other radicals has been achieved in 1,3-bis-(2-hydroxyphenyl)-1,3-propanedione (bhpph<sub>3</sub>) (**I**) at the methinic carbon by reacting the cobalt complex of this  $\beta$ -diketone with different electrophiles. Scheme 1 shows schematically the reaction, and the chemicals obtained.

Unfortunately, it was only possible to obtain **III**, and even this in poor yield, since both reactions proceeded further to yield the corresponding flavone (Scheme 2).

In addition the reaction of **II** with several other electrophiles, such as  $CH_3-CHBr-Ph$ ,  $BrCH_2-COOEt$ , did not proceed at all. This result and the fact that poor yields of the  $\beta$ -diketones compared to the flavones were obtained urged us to check

TABLE I. Final Atomic Coordinates ( $\times 10^3$ ) ( $\text{Cr} \times 10^4$ ) of  $\text{C}_{45}\text{H}_{33}\text{O}_{12}\text{Cr}$

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cr	72803(6)	16829(7)	97514(8)
O(1)	6896(3)	725(3)	10351(4)
C(1)	6373(4)	-217(4)	9664(5)
C(10)	5722(4)	-470(5)	8573(5)
C(2)	5561(3)	257(4)	8143(5)
O(2)	6087(3)	1178(3)	8596(4)
C(11)	6488(4)	-1005(4)	10082(5)
C(12)	7271(4)	-900(5)	10914(6)
C(13)	7386(5)	-1654(6)	11280(7)
C(14)	6756(6)	-2496(7)	10878(9)
C(15)	5942(5)	-2703(6)	9979(7)
C(16)	5821(4)	-1947(5)	9609(6)
O(12)	7978(3)	-28(4)	11437(4)
C(21)	4780(4)	22(5)	7142(5)
C(22)	4618(4)	789(6)	6744(6)
C(23)	3863(6)	546(8)	5777(8)
C(24)	3263(6)	-436(8)	5237(8)
C(25)	3392(6)	-1183(8)	5641(8)
C(26)	4147(5)	-942(6)	6605(6)
O(22)	5140(3)	1754(4)	7238(5)
O(3)	6741(3)	3004(3)	11159(4)
C(3)	6552(4)	3930(4)	11247(5)
C(30)	6715(4)	4126(5)	10267(6)
C(4)	7246(4)	3467(4)	9231(5)
O(4)	7625(3)	2569(3)	9050(4)
C(31)	6188(4)	4809(5)	12489(6)
C(32)	5769(5)	5774(5)	12724(7)
C(33)	5485(6)	6558(6)	13952(8)
C(34)	5638(6)	6403(7)	14933(8)
C(35)	6038(7)	5481(8)	14752(7)
C(36)	6305(5)	4642(6)	13515(6)
O(32)	5560(5)	5967(5)	11775(6)
O(32)	6452(19)	3724(24)	13387(21)
C(41)	7458(4)	3772(5)	8292(6)
C(42)	8125(4)	3255(5)	7422(6)
C(43)	8320(5)	3590(6)	6577(6)
C(44)	7855(6)	4435(7)	6601(7)
C(45)	7187(7)	4945(8)	7429(8)
C(46)	6983(6)	4619(7)	8248(7)
O(42)	8624(3)	2415(4)	7328(5)
O(5)	8448(2)	2096(3)	10907(3)
C(5)	9286(4)	1763(4)	10605(5)
C(50)	9475(4)	968(5)	9326(5)
C(6)	8789(4)	370(4)	8248(5)
O(6)	7885(2)	429(3)	8342(3)
C(51)	10047(4)	2284(4)	11733(5)
C(52)	9834(5)	3042(5)	13051(5)
C(53)	10567(6)	3514(6)	14086(6)
C(54)	11477(5)	3268(6)	13872(7)
C(55)	11686(5)	2537(7)	12580(8)
C(56)	11000(4)	2061(5)	11542(6)
O(52)	8962(4)	3356(5)	13374(5)
C(61)	9033(4)	-404(5)	6892(5)
C(62)	8342(4)	-1095(5)	5828(5)
C(63)	8602(6)	-1761(6)	4564(6)
C(64)	9532(5)	-1754(7)	4313(7)
C(65)	10210(5)	-1084(7)	5348(7)

(continued)

TABLE I. (continued)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(66)	9975(4)	-426(6)	6604(6)
O(62)	7421(3)	-1180(4)	5967(4)
C(1)	-420(16)	5011(20)	859(13)
C(2)	363(18)	4246(16)	304(19)
C(3)	767(14)	4242(14)	-548(20)
C(4)	-707(20)	4892(22)	1577(41)

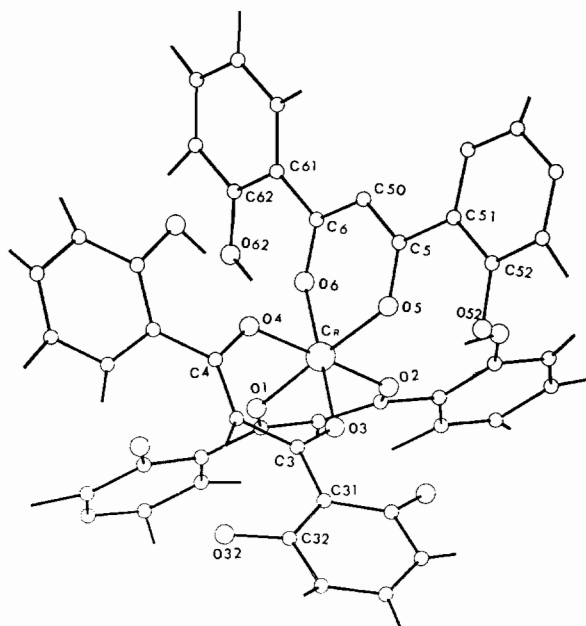
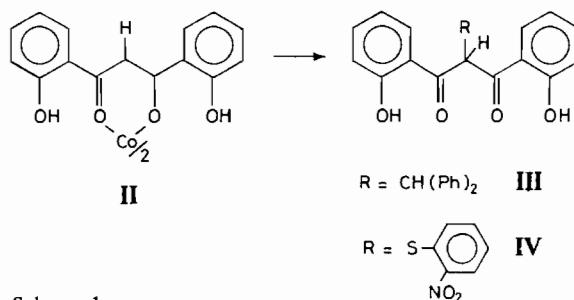
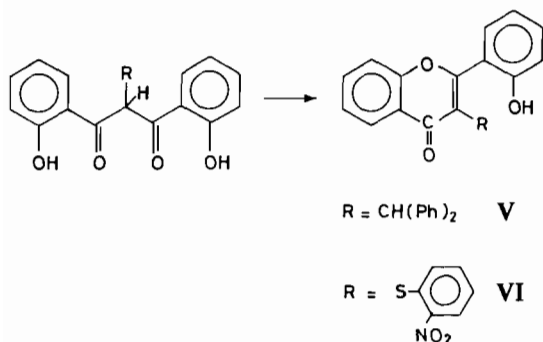


Fig. 1. Molecular configuration and labelling scheme for  $\text{Cr}(\text{bhppH}_2)_3$ .



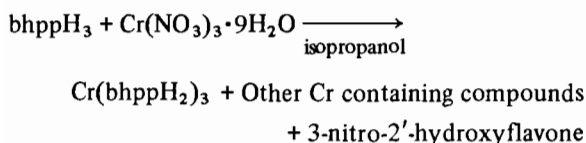
Scheme 1.

for other solvents where the reaction could proceed. According to the literature, appropriate solvents for this kind of reaction are  $\text{CHCl}_3$  and benzene. Since  $\text{M}(\text{bhppH}_2)_2 \cdot 2\text{ROH}$  are insoluble in these solvents, we tried to employ other complexes. It is known that, in general, the tris  $\beta$ -diketone complexes are soluble in these type of solvents. However, several attempts at synthesizing  $\text{Cr}(\text{bhppH}_2)_3$ , starting from  $\text{CrX}_3$  ( $\text{X} = \text{Cl}, \text{BF}_4$ ) failed, yielding in most cases unreacted materials and 2'-hydroxyflavone.



Scheme 2.

The best procedure is indicated in Scheme 3 represented for  $\text{Cr}^{3+}$  but also valid for  $\text{Fe}^{3+}$ .



Scheme 3.

Even in this case, this synthesis produces  $\text{Cr}(\text{bhppH}_2)_3$  (**VII**) in poor quantities, yielding other  $\text{bhppH}_3\text{-Cr}$  containing complexes and organic compounds, among them 3-nitro-2'-hydroxyflavone (**VIII**). The results for  $\text{Fe}^{3+}$  are comparable to these found for  $\text{Cr}^{3+}$ ; both chemicals  $\text{Cr}(\text{bhppH}_2)_3$  (**VII**) and  $\text{Fe}(\text{bhppH}_2)_3$  (**IX**) were appropriate to try the electrophilic reaction.

The strong tendency observed in these  $\beta$ -diketone compounds to eliminate water and rearrange to the corresponding flavone made it necessary to have a smooth method available to destroy the complex, and liberate the substituted  $\text{bhppH}_2$  ligand.

We chose the  $\text{Fe}^{3+}$  complex because of the high stability constant that presents with  $\text{SCN}^-$  and the fact that the destructive reaction could easily be followed.

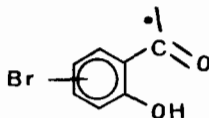
Reaction of  $\text{Fe}(\text{bhppH}_2)_3 \cdot 2\text{H}_2\text{O}$  with *N*-bromosuccinimide (NBS) in chloroform for 10 min, followed by treatment of the solution with aqueous  $\text{NH}_4\text{SCN}$  yielded after work-up, 3-bromo-2'-hydroxyflavone (**X**) and some dibrominated derivatives of  $\text{bhppH}_3$ , altogether with variable quantities of **I** and 2'-hydroxyflavone.

As indicated, the bromination on the  $\text{Fe}(\text{bhppH}_2)_3$  compound, yielded mostly dibrominated flavone derivatives. To our understanding dibromination does not take place on the same carbon, but on the methinic and probably on the phenyl ring. We base this on the fact that dibromination on the methinic carbon would imply a destruction of the  $\text{Fe}(\text{Br}_2\text{-bhppH}_2)_3$  complex since no enolic form would be possible, and it has not been observed.

TABLE II. Intramolecular Bond Distances (Å) and Angles (deg) for  $\text{Cr}(\text{bhppH}_2)_3$ 

Bond distances			
O(1)–Cr	1.951(5)	O(2)–Cr	1.968(4)
O(3)–Cr	1.944(3)	O(4)–Cr	1.943(5)
O(5)–Cr	1.949(4)	O(6)–Cr	1.950(3)
C(1)–O(1)	1.295(6)	C(10)–C(1)	1.427(8)
C(11)–C(1)	1.464(11)	C(2)–C(10)	1.402(11)
O(2)–C(2)	1.294(7)	C(21)–C(2)	1.475(8)
C(12)–C(11)	1.397(8)	C(12)–O(12)	1.392(7)
C(22)–C(21)	1.425(13)	O(22)–C(22)	1.332(9)
C(3)–O(3)	1.288(8)	C(30)–C(3)	1.406(11)
C(31)–C(3)	1.484(7)	C(4)–C(30)	1.391(8)
O(4)–C(4)	1.298(8)	C(41)–C(4)	1.480(11)
C(32)–C(31)	1.386(10)	O(32)–C(32)	1.343(13)
C(42)–C(41)	1.383(8)	C(42)–O(42)	1.348(9)
C(5)–O(5)	1.300(6)	C(50)–C(5)	1.391(7)
C(51)–C(5)	1.498(7)	C(6)–C(50)	1.398(7)
O(6)–C(6)	1.305(6)	C(61)–C(6)	1.480(7)
C(52)–C(51)	1.428(7)	O(52)–C(52)	1.346(8)
C(62)–C(61)	1.410(7)	O(62)–C(62)	1.351(7)
Bond angles			
O(2)–Cr–O(1)	88.5(2)	O(3)–Cr–O(1)	88.5(2)
O(3)–Cr–O(2)	92.1(1)	O(4)–Cr–O(1)	176.5(1)
O(4)–Cr–O(2)	88.6(2)	O(4)–Cr–O(3)	89.3(2)
O(5)–Cr–O(1)	87.7(2)	O(5)–Cr–O(2)	176.1(2)
O(5)–Cr–O(3)	89.2(1)	O(5)–Cr–O(4)	95.1(2)
O(6)–Cr–O(1)	90.6(2)	O(6)–Cr–O(2)	89.9(1)
O(6)–Cr–O(3)	176.1(2)	O(6)–Cr–O(4)	87.4(2)
O(6)–Cr–O(5)	89.0(1)	C(1)–O(1)–Cr	126.0(4)
C(10)–C(1)–O(1)	122.2(7)	C(11)–C(1)–O(1)	115.7(5)
C(2)–C(10)–C(1)	125.0(5)	O(2)–C(2)–C(10)	122.3(5)
C(21)–C(2)–O(2)	115.6(6)	C(2)–O(2)–Cr	127.8(5)
C(3)–O(3)–Cr	128.5(4)	C(30)–C(3)–O(3)	122.8(5)
C(31)–C(3)–O(3)	115.4(6)	C(4)–C(30)–C(3)	124.9(7)
O(4)–C(4)–C(30)	122.5(7)	C(41)–C(4)–O(4)	115.1(5)
C(4)–O(4)–Cr	127.4(4)	C(5)–O(5)–Cr	129.0(3)
C(50)–C(5)–O(5)	123.4(4)	C(51)–C(5)–O(5)	115.6(4)
C(6)–C(50)–C(5)	124.5(5)	O(6)–C(6)–C(50)	123.6(4)
C(61)–C(6)–O(6)	114.1(4)	C(6)–O(6)–Cr	126.1(3)

On the other hand, the existence in some of the ME spectra of these compounds of base peaks at 199(99.5%) and 201(100%) attributed to



supports our supposition. This result together with the complexing properties of **III** (see later) discouraged pursuit with these electrophilic reactions.

The fact that we had obtained mostly dibrominated compounds posed serious doubts about the extent with which the bromination reaction had taken place. To observe the effects on a non-phenylic  $\beta$ -diketone we followed Collman's proce-

cedure to get tris-(3-bromo-2,4-pentanedionate)iron-(III). Treatment of this solid with  $\text{NH}_4\text{SCN}$ , as before, yielded 3-bromo-2,4-pentanedione but mostly, dibrominated-2,4-pentanedione. (We believe 1,3-dibromo-2,4-pentanedione.)

As mentioned earlier, our interest consisted in obtaining soluble heterotrimetallic complexes based on the  $\text{bhppH}_3$  derivatives.

In contrast to what happened when  $\text{bhppH}_3$  was mixed with  $\text{M}(\text{AcO})_2 \cdot x\text{H}_2\text{O}$  when  $\text{M}(\text{bhppH}_2)_2 \cdot 2\text{ROH}$  complexes were obtained, no reaction was observed upon the mixing of **III** with these type of salts. To get complexation, trimethylamine was added and, in this situation, a solid separated in both cases. Analysis of these solids indicated a composition approximated to  $\text{M}_3(\text{dpmhbpp})_2 \cdot x\text{ROH}$ . These compounds solubilized in pyridine, yielding after a few days solids which were recrystallized in  $\text{CH}_2\text{Cl}_2$ .

Crystals with appropriate dimensions to run an X-ray diffraction analysis were obtained in both cases. Unfortunately, only twin crystals were obtained in every attempt. The analysis of these compounds corroborated the stoichiometry  $\text{M}_3(\text{dpmhbpp})_2 \cdot 6\text{py}$  (**XI–XII**).

As a conclusion, our expected target of an increased solubility with maintenance of the selectivity upon substitution of the methynic hydrogen by other groups has, in part, failed. Even though a higher solubility has been obtained, there has also been a loss of selectivity. This has probably been due to a decrease of the enolic *versus* the diketonic form upon the substitution. According to data in the literature it may be possible only with chlorine to get a selectivity comparable to that of the  $\text{bhppH}_3$  ligand, however, in this case the steric factor would not be too favorable.

## Supplementary Material

Tables of hydrogen coordinates, anisotropic temperature factors, and measured and calculated structure factors are available from the authors.

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