



SYNTHESIS AND CHARACTERIZATION OF COBALT BIS - β DIKETONATES

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ABSTRACT:

Bis β diketones have been synthesized by employing Baker Venkantraman Rearrangement on esters (o-aryloxy/heteroaryloxyacetophenones). The transition metal complexes have been synthesized by simple refluxing the ligand with the transition metal salts. The synthesized compounds were characterized by analytical techniques viz: IR, NMR, Mass and elemental analysis.

Keywords: Bis β diketones, Baker Venkantraman Rearrangement, metal complexes.

INTRODUCTION:

β -Diketones are among the most studied ligands in the chemistry of metal complexes¹⁻³ The nature of bonding and chelation was elucidated by Werner and Morgan⁴⁻⁵. β -diketonates have been exploited as building units in supramolecular⁶⁻¹⁵. β -Diketones have a wide range of uses ranging from metal extraction by chelation, to biomedical applications like as antibacterial antibiotics, to being used as a ligand in metal complexes for catalysis¹⁶⁻²⁰. The β -diketonates form a versatile class of chelating ligands²¹ whose uses in transition metal chemistry has been appreciated for almost 120 years²². Bis (β -diketonate) ligands that form complexes in which both diketones are bonded to the same metal center have not been previously known. Instead, linked bis (β -diketonates) have been used exclusively to construct dimetallic or polymetallic architectures.

β -Diketone hydrazone derivatives are known to act as good chelating agents. The interest in studying these compounds and their metal complexes arises from their behaviour as efficient antituberculous agents²³ Furthermore, some hydrazones are used as quantitative analytical reagents, especially in colorimetric and fluorimetric determinations of metal ions. Some β -diketonato complexes of

titanium (IV) showed activities against tumors. β -diketonates have a wide range of uses in metal extraction by chelation. 1,3-Diketones are very important compounds in organic chemistry, because they exhibit some biological activities, such as antioxidants, antitumors, and antibacterial activities and are also key intermediates to various heterocyclic compounds²⁴⁻²⁵. Europium (III) β -diketonates have excellent luminescent property²⁶.

Present Work

The present work describes the preparation 3,3'-(4,6-Dihydroxy-1,3-phenyl)bis(1-aryl/heteroaryl propane 1,3-diones) and its transition metal complexes. The title compound was synthesized by employing Baker Venkantraman Rearrangement on esters (o-aryloxy/heteroaryloxyacetophenones). The synthesized compounds were characterized by analytical techniques viz: IR, NMR, Mass and elemental analysis.

MATERIAL METHODS:

A using (KBr) disc on Perkin-Elmer spectrum Rx-I II the elemental analyses were done using the Perkin Elmer 2400 CHN analyzer. FT-IR spectra were recorded spectrometer. H NMR were recorded on Bruker AC-300 F (300 MHz) NMR spectrometer by using DMSO-*d* and CDCl₃ as solvent and tetramethylsilane as an internal standard. Mass

spectra were recorded on 70-S Mass spectrometer using m-nitro benzyl alcohol (NBA) matrix.

4,6- Diacetylresorcinol (resdiacetophenones).

Resorcinol (20.0g, 0.181mole) was dissolved in (42.65g, 0.4178 mole) of acetic anhydride (63.16g, 0.4644 mole) of ZnCl₂ was added and the mixture was heated. After 3 hours of the mixture at 150° to 160°C, 4,6-diacetylresorcinol crystallized out. After cooling, 25g of water was added for hydrolyzing the remaining acetic anhydride, then 40g of methanol was added and, for growing crystals, the resulting mixture was heated under reflux for 30 minutes, then cooled and subjected to solid-liquid separation. The solid was washed with 168g of methanol and then dried where by 26.03g (0.1340 mole) of 4,6-diacetylresorcinol was obtained. The yield was 73.8 % on the resorcinol basis.

1,3-Dibenzoyloxy-4,6-diacetophenone:4,6-

Diacetylresorcinol (resdiacetophenones) (0.1 mole) and dry pyridine (10ml), Benzoyl chloride (0.2 mole) was added slowly maintaining the temp. below 20°C. The reaction mixture was kept overnight and poured on a mixture of ice and HCl. Generally a solid compound separated which was washed with water and dilute NaOH solution and crystallized from ethanol. The yield is 70% m.p- 90°C.

3,3'-(4,6-dihydroxy-1,3-phenyl) bis (1-phenyl propane-1,3dione).

1,3-Dibenzoyloxy-4,6-diacetophenones (0.005moles) was dissolved in 4ml of DMSO. To that solution powdered NaOH (2g) was added with vigorous stirring for about five minutes. The stirring was continued for about 5 min further. The reaction mixture was then cooled and poured on cold water. The pale yellow solid product obtained was washed with water dried and crystallized from alcohol. The yield 67% and m.p 121°C

3, 3'-(4,6-Dihydroxy-1,3-phenyl)bis[(1-aryl/heteroaryl propane1, 3-dionate)] Co(II) (2a). A mixture of 2g (5×10^{-3}) 3,3'-(4,6-dihydroxy-1,3-phenyl) bis (1-phenyl propane-1,3dione) and 0.49g (2.5×10^{-3}) cobalt (II) acetate and 50ml of anhydrous ethanol was stirred at 50-60°C for 3h. The pink solid obtained was washed with ethanol and then with ethyl acetate. The yield was 62.63%. In the same way, all the other cobalt (II) metal complexes **3b-f** were prepared by adopting the same procedure.

RESULT & DISCUSSION :

1,3-Dibenzoyloxy-4,6-diacetophenone undergoes Baker-Venkataraman rearrangement to afford pale yellow needles of 3,3'-(4,6-dihydroxy-1,3-phenyl) bis (1-phenyl propane-1,3dione)

The structure was further confirmed by the spectral analysis: Ketone group test : It gives positive test for ketone group IR (KBr): 3568 (-OH); higher than that of its metal complexes for most of the 3061 (=C-H); 1655 (-C=O); 1589 (C=C); 29261 (Ar-H); ¹H bacteria. NMR (DMSO-d₆) : 12.95(s, 1H), 12.72 (s, 1H), 3.19(s, 1H), 8.89(s, 1H), 8.84 (d, 2H), 7.10-8.17 (m, 12H), C₂₄H₁₈O₆ 7.26 (d, 1H), 6.92 (d, 1H), 7.02 (s, 1H); MS (EI, 70eV): m/z (%) 281 (M⁺, 100), Anal. Calcd. for C₂₄H₁₈O₆ : C, 71.60; H, 4.46. Found: C, 71.12; H, 4.81. In the ¹H NMR Spectra it gives characteristic peak at 12.95 which is enolic proton and at 12.02 the formation of -diketones. The compound in enolic drugs form is more stable than that of ketonic one.

The complex of synthesized compound **2** gives pink coloured Co (II) -diketonate **4a** in high yield. The structure was then confirmed by the spectral analysis

IR (KBr): 3405cm⁻¹ (OH), ; higher than that of its metal complexes for most of the 1590 (C=C), 2936 (=C-H); (C-H), 1532(-C=O) NMR (DMSO-d₆) : 11.95(s, 1H), 12.72 (s, 1H), 3.19(s, 1H), 7.10-8.17 (m, 12H), 7.26 (d, 1H), 6.3 (d, 1H), Anal.

Calcd. $C_{48}H_{40}Co_2O_{14}$ for C H Co: C, 60.13; H, 4.17; Co, 15.2 ; Found : C, 60.07, H, 4.11, Co, 10.43 The lowering of C=O stretch, metal – oxygen stretch at 484cm^{-1} and absence of enolic proton between δ 14-16 ppm confirms the formation of complex of the ligand **1a** with cobalt (II) having molecular formula $C_{48}H_{40}Co_2O_{14}$. Similarly, other transition metal complexes were prepared by the same method. The ligand and its metal⁸; complexes are quite stable. All the complexes are insoluble in water but soluble in acetone, Methanol and DMSO The complexes are non-electrolytic in nature

CONCLUSION :

Thus, on the basis of the study results, it is concluded that there is noticeable change in the number of fruits on Cotton, and Tur crops in the study area.

ACKNOWLEDGMENT:



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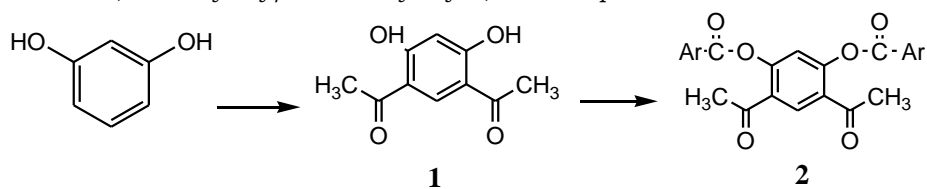
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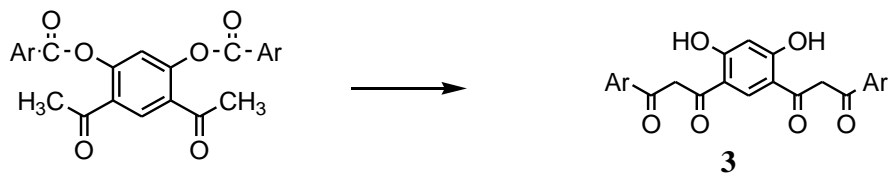
**Elemental Analysis of 3,3'-(4,6-Dihydroxy-1,3-phenyl)bis
[(1-aryl/heteroaryl propane-1,3-dione)] Co (II) 2a-f**

Compound	Colour with FeCl ₃	Ar-Aryl	Empirical formula	Yield	Calc. (found)			%M Calc. (found)	Decomposition Temp. °C
					C	H	N		
2a	Red	C ₆ H ₅	C ₄₈ H ₄₀ O ₂ O ₁₄	62.63	60.13 (60.07)	4.17 (4.11)	–	15.2 (10.43)	580
2b	Brown	4-OCH ₃ C ₆ H ₅	C ₅₂ H ₄₈ O ₂ O ₁₈	64.94	57.89 (57.85)	4.45 (4.40)	–	10.75 (9.58)	420
2c	Red	4-ClC ₆ H ₄	C ₄₈ H ₃₆ O ₂ O ₁₄ Cl ₄	63.90	52.64 (52.60)	3.28 (3.25)	–	9.97 (7.21)	430
2d	Brown	4-CH ₃ C ₆ H ₄	C ₅₂ H ₄₈ O ₂ O ₁₄	69.10	61.56 (61.52)	4.73 (4.69)	–	10.95 (10.10)	450
2e	Red		C ₄₀ H ₃₂ O ₂ O ₁₄ S ₂	65.43	52.34 (52.30)	3.48 (3.42)	–	10.39 (10.2)	430
2f	Red		C ₄₄ H ₃₂ O ₂ O ₁₄ N ₂	63.22	55.63 (55.60)	3.37 (3.33)	5.05 (5.00)	12.02 (11.62)	480

Scheme: Synthesis of ligand and its metal complexes.

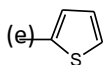
1. 1,3-Diaroyloxy/heteroaryloxy-4,6-diacetophenones **2**

2. 3',3'-(4,6-dihydroxy-1,3-phenyl) bis (1-aryl/heteroaryl propane-1,3diones)



Ar = Ar₁
= Ar₁

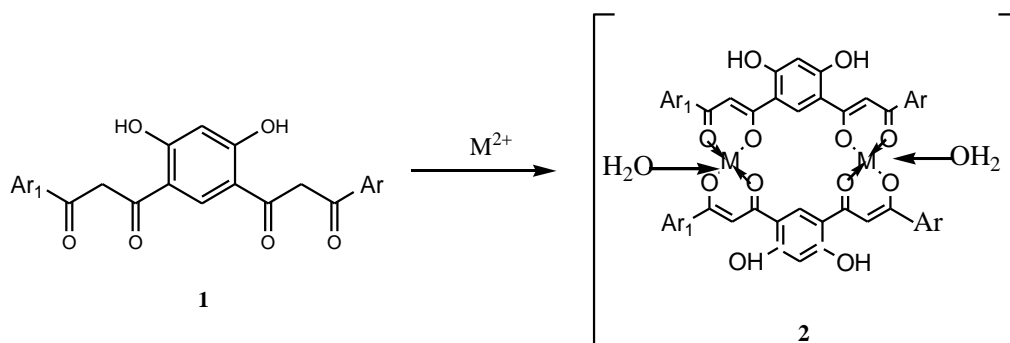
OCH₃C₆H₄



3.

(f)

(a) C₆H₅ Ar
(b) 4-CH₃C₆H₄
(c) 4-
(d) 4-ClC₆H₄



M = Co(II)