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Synthesis and Characterization of Bis –B Diketones and Its Metal Complexes

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Abstract

3,3'-(4,6-Dihydroxy-1,3-phenyl)bis(1-aryl/heteroaryl propane1,3-diones) and transition metal complexes have been synthesized. Bis –β diketones have been synthesized by employing Baker Venkantraman Rearrangement on esters (o-aroyloxy/heteroaroyloxyacetophenones)The synthesized compounds were characterized by analytical techniques viz: IR, NMR, Mass and elemental analysis. The thermal stability ofthenewly synthesized metal complexes have been studied.

Keywords: Bis –β diketones , Baker Venkantraman Rearrangement, metal complexes, thermo gravimetric analysis

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Introduction:

B-Diketonates are among the most studied ligands in the chemistry of metal complexes[1-2]. β-diketonates have been exploited as building units in supramolecular design[3-4]. Tetra acetylethane is the simplest tetraketone with two separated β-diketonate functions[5-6]. β-Diketones have a wide range of used ranging from metal extraction by chelation, to biomedical applications like as antibacterial antibiotics, to being used as a ligand in metal complexes for catalysis[5-6]. The β-diketonates form a versatile class of chelating ligands [5]whose uses in transition metal chemistry has been appreciated for almost 120 years[6].β-Diketonehydrazone derivatives are known to act as good chelating agents[7-8].The interest in studying these compounds and their metal complexes arises from their behaviour as efficient antituberculous agents [9] Furthermore, some hydrazones are used as quantitative analytical reagents, especially in colorimetric and fluorimetric determinations of metal ions [10-11]. Some β-diketonatocomplexs of titanium (IV) showed activities against tumors[12] . Some β-diketonate manganese complexes show extraordinary structures and interesting magnetic properties[13]. Owing to their effective properties with respect to extracting metal ions, β-diketone compounds have attracted most interest in recent decades. They can also be used in laser materials, proton NMR shift reagents, MOCVD, the petroleum industry and analytical chemistry[14-15]. There are only a few reports on poly-β-diketone complexes [16].Diketones are well known to have two forms, that is enol and keto forms. One of the most interesting properties is the conversion between the two forms, which was termed as keto-enol tautomerism[17].The enol form is more stable than the keto form in a solution, and the tautomeric equilibrium can be affected by various factors such as solvent polarity[18] substitution groups[19],pH values [20] and UV[21] light irradiation. 1, 3-Diketones are very important using (KBr) disc on Perkin-Elmer spectrum Rx-I

Present work

The present work describes the preparation 3,3'-(4,6-Dihydroxy-1,3-phenyl)bis(1-aryl/heteroaryl propane1,3-diones) and its transition metal complexes . The title compound was synthesized by employing Baker

VenkantramanRearrangement on esters (o-aroyloxy/heteroaroyloxyacetophenones) .The synthesized compounds were characterized by analytical techniquesviz: IR, NMR, Mass and elemental analysis. The thermal stability of the newly synthesized metal complexes have been studied.

Materials and Method:

A using (KBr) disc on Perkin-Elmer spectrum Rx-I ll the elemental analyses were done using the Perkin Elmer 2400 CHN analyzer. FT-IR spectra were recorded spectrometer. H NMR were recorded on Brucker AC-300 F (300 MHz) NMR spectrometer by using DMSO-*d* and CDCl 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)[84]**.** Resorcinol (20.0g, 0.181mole) was dissolves in (42.65g, 0.4178 mole) of acetic anhydride (63.16g, 0.4644 mole) of ZnCl2 was added and the mixture was heated. After 3hours 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 46-diacetylresorcinol was obtained. The yield was 73.8 % on the resorcinol basis.

2. 1,3-Dibenzoloxy-4,6-diacetophenone:4,6-Diacetylresorcinol (resdiacetophenones) (0.1 mole) and dry pyridine (10ml), Benzoyl chloride (0.2 mole) was added slowly maintining 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. 3,3'-(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

4. 3'-(4,6-Dihydroxy-1,3-phenyl)bis[(1-aryl/heteroaryl propane1, 3-dionate)] Cu(II) (2a). A mixture of 2g (5×10^{-3}) of 3,3'-(4,6-dihydroxy-1,3- phenyl) bis (1-phenyl propane-1,3dione) and0.52g(2.5×10^{-3}) copper (II)acetate and 50ml of anhydrous ethanol was stirred at 50-60^{o}C for 3h. The green solid obtained was washed with ethanol and then with ethyl acetate. The yield was found to be 68.96%. Similarly, the complexes of Cobalt, Nickel, Manganes and Zinc were prepared by the same method .

Result and Discussion:

1,3-Dibenzoloxy-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 gaves positive test for ketone groupIR (KBr): 3568 (-OH); higher than that of its metal complexes for most of the3061 (=C-H); 1655 (-C=O); 1589 (C=C); 29261 (Ar-H);.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), $C_{24}H_{18}O_6$7.26 (d, 1H), 6.92 (d, 1H), 7.02 (s, 1H); MS (EI, 70eV): m/z (%) 386 (M^+, 100), Anal. Calcd.for C H O : C, 71.60; 15 12 4

H, 4.46. Found: C, 71.12; H, 4.81. In the 1H NMR Spectra it gives characteristic peak at 12.95 which)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 3 gives green coloured Cu (II) -diketonate 4a in high yield. The structure was then confirmed by the spectral analysis

IR (KBr): 3405(-OH); higher than that of its metal complexes for most of the

3061 (=C-H); 1718 (-C=O); 1580 (C=C); 29221 (Ar-H); 1H NMR (DMSO-d6) : 12. 95(s, 1H), 12.72 (s, 1H), 3.19(s, 1H),7.10-8.17 (m,12H),..26 (d, 1H), 6.3 (d, 1H), Anal. Calcd $C_{48}H_{40}Cu_2O_{14}$ for C H Cu: C, 61.47; H,3.94;Cu,16.50 ;Found :C,61.35,H,3.85,Cu,15.94

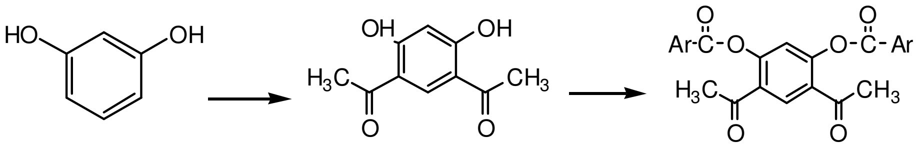
Similarly, other transition metal complexes were prepared by the same method. The ligand and its metal8; complexes are quite stable. All the complexes are insolublein water but soluble in acetone, Methanol and DMSO The complexes are non-electrolytic in nature

Thermogravimetric Analysis:

All thermal analyses were done on Perkin Elmer SII, Diamond TG/DTAThermogravimetric analyzer at VNIT, Nagpur. TheThermogravimetric curves of the synthesized complexes were recorded between 300C -10000C in air as medium. The TGA curves of all the complexes are almost similar and indicate a continuous weight loss till a stable metal oxide is formed. Weight loss of 3.21% - 3.86% between 150°C - 180°C has been observed for copper, cobalt,complex which indicate the presence of two molecules of water of coordination. On further increasing the temperature, no weight loss takes place probably due to the formation of stable metal oxides.

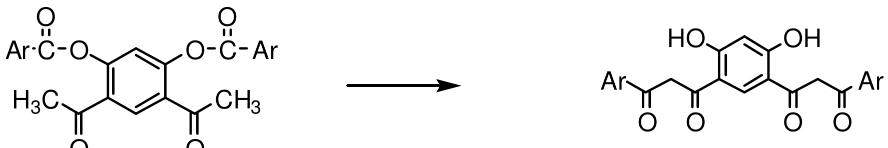
Scheme: Synthesis of ligand and its metal complexes.

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



1 **2**

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



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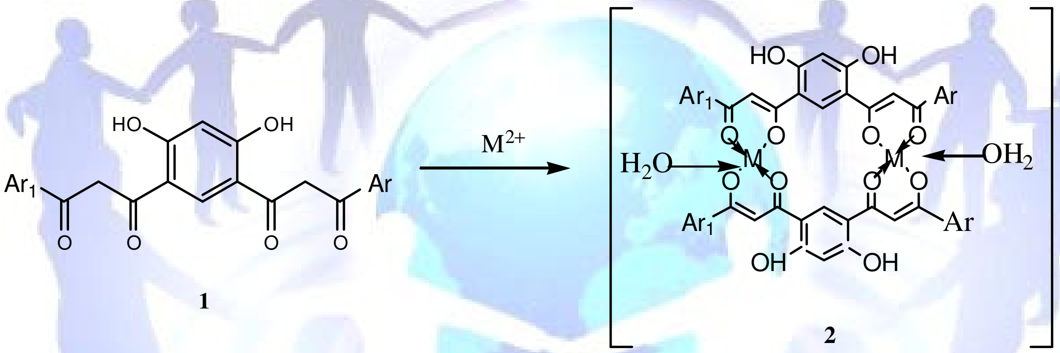
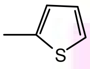
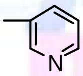


Ar =Ar$_1$ (a) C_6H_5 (b) 4-$CH_3C_6H_4$

(c) 4-$OCH_3C_6H_4$ (d)4-ClC_6H_4

(e) 

(f) 

M = Cu(II),Co(II)

Table. 1- Thermal data of the complexes

Sr.no	Complex	Coordination water (%) Obs (calc)	Decomposition Temperature (°C)	% Weight loss Obs (calc)	Residue comp
1	$C_{48}H_{40}Cu_2O_{14}$	3.75 (3.86)	200	16.44(16.50)	CuO
2	$C_{48}H_{40}Co_2O_{14}$	3.70(3.76)	230	14.90(15.01)	Co_2O_3

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