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Studies on Diazocoupling Products of Dioxomolybdenum (VI) Chelates of β -diketones

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Abstract: A number of diazocoupling products of molybdenum (VI) chelates of β -diketones with various types of aryldiazonium ions have been prepared. Aryldiazonium ions are obtained through the diazotization of aniline and substituted aniline using sodium nitrite and hydrochloric acid. The prepared diazocoupled products were studied by their analytical data, magnetic moment, molar conductance, electronic, infrared and ¹HNMR spectral studies. The presence of $\nu_{N=N}$ mode in the IR spectra and absence of methane proton signal in the ¹HNMR spectra of the prepared diazocoupled products indicate the occurrence of diazocoupling reaction. The molar conductance values indicate the non-electrolytic nature of the diazocoupled products. The electronic spectra and the dia magnetic behavior are indicative of the presence of +6 oxidation state of molybdenum. The structures of the synthesized diazocoupled products of molybdenum (VI) are likely to be octahedral.

Key words: Aryldiazonium ion, electrophilic substitution, β -diketone, ¹HNMR spectrophotometer

INTRODUCTION

The chemistry of complex compounds has attracted much attention due to their various uses in biological processes and homogeneous catalysis^[1,2]. β -diketones have the property of forming stable ions as a result of enolisation followed by ionization. These β -ketoenolate ions form very stable chelates complexes with a great range of metal. Among the commonest types of diketo complexes are those with the stoichiometric $M(\text{diketo})_3$ and $M(\text{diketo})_2$. The former all have structures based on an octahedral disposition of the six oxygen atoms. The tris chelate molecules then actually have D_3 symmetry and exist as enantiomers. Substances of composition $M(\text{diketo})_2$ are almost invariable oligometric, unless the R- groups are very bulky ions, such as $(\text{CH}_3)_3\text{C}$ -. These facts shows that in $M(\text{diketo})_2$ molecules, the Mo atoms are coordinately unsaturated^[3], they prefer a coordination number of +6 (or at least +5) and attain such coordination numbers by sharing of oxygen atoms.

β -diketonates like acetylacetone (acacH) and benzoylacetone (bzacH) having at least one hydrogen on the α -carbonyl atom and capable of exhibiting keto-enol tautomerism^[4] react with dioxomolybdenum (VI) cation, MoO_2^{2+} to form $\text{MoO}_2(\text{acac})_2$ complexes^[5]. β -diketonate complexes of dioxomolybdenum (VI) has been used for

synthesis of various types of complexes as starting materials^[6]. Aryldiazonium ion is a dominant electrophile and the diazocoupling reaction has been recognized as an electrophilic substitution reaction^[7]. Metal-1, 3 diketonates are known to undergo many electrophilic substitution reactions (such as halogenation and nitration) typical of aromatic compounds in view of the quasi-aromatic $\text{C}_3\text{O}_2\text{M}$ ring system presents in these compounds^[8-10]. The substitution reaction of aryldiazonium ion on metal [Cu(II), Ni(II), Pd(III) and Cr(III)] chelates of β -diketonates have also been reported^[11].

The aryldiazonium ion, 4-chloro aryldiazonium ion, 4-bromo aryldiazonium ion, 4-nitro aryldiazonium ion, 2,5-dimethoxy aryldiazonium ion and α -naphthalene aryldiazonium ion have been synthesized and these ions are used for the substitution reaction with dioxomolybdenum (VI) chelates of acetylacetone and benzoylacetone in this study. In the present study attempts have been made in order to characterize the diazocoupling reaction of these diazonium ions with $\text{MoO}_2(\text{acac})_2$ and $\text{MoO}_2(\text{bzac})_2$, the interpretation of the formula of prepared diazocoupled products with geometrical configuration were also focused in the present investigation.

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MATERIALS AND METHODS

The diazocoupling reaction of aryldiazonium ions with dioxomolybdenum (VI) chelates of β -diketonates were performed by three steps.

Step A: Preparation of metal β -diketonate

A modified procedure^[5] was followed to prepare $\text{MoO}_2(\text{acac})_2$ and $\text{MoO}_2(\text{bzac})_2$ as starting materials.

Step B: Preparation of aryldiazonium ion

Benzoylacetone was used instead of acetylactone for preparing $\text{MoO}_2(\text{bzac})_2$. Aryldiazonium salts were obtained through the diazotization of arylamine using sodium nitrite in mineral acid ($\text{HCl}/\text{H}_2\text{SO}_4$) at $0\text{--}5^\circ\text{C}$ ^[12].

Step C: Diazocoupling reaction upon metal β -diketonates

To a solution of the metal 1,3-diketonates (0.0015 mol) in methanol (10 mL) kept below 5°C in an ice salt bath, a cold aqueous solution of the diazonium salt (0.003 mol) was added slowly with vigorous stirring. A solution of NaOH (10^{-3}M) was used to maintain the pH of the mixture between 8 and 9. Stirring the mixture slowly to attain room temperature. The precipitation product was filtered, washed with distilled water, sucked dry, recrystallized from hot ethanol and dried under vacuum over silica gel. The diazocoupled products are obtained the following:

1. $\text{MoO}_2[\text{Arylazo-acac}]_2$
2. $\text{MoO}_2[4\text{-bromo-arylazo-acac}]_2$
3. $\text{MoO}_2[2,5\text{-dimethoxy-arylazo-acac}]_2$
4. $\text{MoO}_2[4\text{-nitro-arylazo-acac}]_2$
5. $\text{MoO}_2[4\text{-chloro-arylazo-acac}]_2$
6. $\text{MoO}_2[\alpha\text{-naphthylazo-acac}]_2$
7. $\text{MoO}_2[4\text{-chloro-arylazo-bzac}]_2$
8. $\text{MoO}_2[2,5\text{-dimethoxy-arylazo-bzac}]_2$
9. $\text{MoO}_2[[\alpha\text{-naphthylazo-bzac}]_2$
10. $\text{MoO}_2[4\text{-nitro-arylazo-bzac}]_2$

JNM-PM \times 60 NMR spectrometer was used for ^1H NMR studies. Magnetic measurements were made with a Curie-Chenevean balance. The infrared spectrum was recorded in Nujol mull on a Shimadzu IR-470 spectrophotometer.

RESULTS AND DISCUSSION

The prepared diazocoupled products are found colored and amorphous powder in nature. The analytical and physical data for the prepared diazocoupled products are shown in Table 1.

The analytical data indicate that substitution has occurred on both the chelate rings of $\text{MoO}_2(\text{acac})_2$ and $\text{MoO}_2(\text{bzac})_2$ and the products have 2:1 stoichiometry. For the diazocoupled products of dioxomolybdenum (VI) chelates of β -diketonates, the regions of major stretching modes are $\nu_{\text{Mo=O}}$, $\nu_{\text{C-N}}$, $\nu_{\text{C=C}}$, $\nu_{\text{C=O}}$, $\nu_{\text{N=N}}$, $\nu_{\text{C-O}}$ and $\nu_{\text{Mo-O}}$. The Mo=O provide structural information about the coordination environment of molybdenum group. The tentative assignments of some characteristic infrared peaks of various diazocoupled products are listed in Table 2. The presence of $\nu_{\text{N=N}}$ modes in IR-spectra of the prepared diazocoupled products indicate that the diazocoupling reaction has occurred between the component reagent.

The most characteristic feature of the prepared diazocoupled products are sharp and strong (O=Mo=O) stretching frequency observed in their IR-spectra at $900\pm 50\text{ cm}^{-1}$ in the case of a trans- MoO_2 group and two IR bands in the case of a cis- MoO_2 group^[13,14] due to the $\nu_{\text{sym}}(\text{O=Mo=O})$ and $\nu_{\text{asym}}(\text{O=Mo=O})$ stretches, respectively. The $\nu_{\text{Mo=O}}$ serves as a diagnostic tool for the identification of the molybdenyl oxygen in the dioxomolybdenum (VI) complexes, the MoO_2 moiety prefers to form a cis- MoO_2 structure due to the maximum utilization of the d-orbital for bonding and even MoO_2 - (porphyrinate)^[15] displays a cis-configuration of dioxo group. The dimeric complexes show two or more vibrational bands in this region. In the dioxomolybdenum (VI) complexes in which there is $\dots\text{Mo=O}\dots\text{Mo=O}\dots$ chain interaction, the $\nu_{\text{Mo=O}}$ frequency occurs at a much lower wave number^[16] 850 cm^{-1} . The reported^[17] ranges for $\nu_{\text{asym}}(\text{O=Mo=O})$ and $\nu_{\text{sym}}(\text{O=Mo=O})$ are $892\text{--}964$ and $840\text{--}925\text{ cm}^{-1}$, respectively. The range $895\text{--}975\text{ cm}^{-1}$ display two bands pattern characteristics of a cis-dioxomolybdenum (VI) center^[18]. The position of these two cis $\nu_{\text{Mo=O}}$ bands in different complexes are found vary from ligand to ligand indicating that the extent of localization of electron cloud on Mo orbital significantly influences the Mo=O bond. The observation of two infrared bands for the prepared diazocoupled products in the region around $900\text{--}960\text{ cm}^{-1}$ shown in Table 2 argues the presence of a cis- MoO_2 group and the absence of any $\dots\text{Mo=O}\dots\text{Mo=O}$ chain structure which indicate the monomeric nature of these products.

^{15}N and ^{18}O isotopes substitution have been used to identify the N and O sensitive vibrations in N-alkyl and N-arylsalicylaldimine and salicylaldeneglycinate complexes^[19]. On the basis of these studies, the bands in the regions $1540\text{--}1600$ and $1370\text{--}1410\text{ cm}^{-1}$ are assigned as due to $\nu_{\text{C=C}}$ and $\nu_{\text{C=N}}$, respectively. It has been reported^[20] that the aromatic C=C vibration at 1585 cm^{-1} for the ligand goes down at 1540 cm^{-1} on chelation and

Table 1: The analytical and physical data for the prepared diazocoupled products

Products	Color	M.P.°C	Yield (%)	Analysis (%), found/(calc.)		
				C	N	Mo
1	Radish	94	30	49.14	10.35	17.50
	Merion			(49.44)	(10.48)	(17.95)
2	Merion	112	35	39.50	7.8	13.40
				(39.17)	(8.09)	(13.86)
3	Chocolate	115	30	47.62	8.15	13.80
				(47.71)	(8.35)	(14.66)
4	Yellow	112	30	42.29	13.09	15.09
	Chocolate			(42.32)	(13.48)	(15.37)
5	Merion	110	40	44.21	8.8	15.20
	Chocolate			(44.06)	(9.29)	(15.90)
6	Blackish	120	35	56.68	8.97	15.09
	Chocolate			(56.79)	(8.83)	(15.12)
7	Chocolate	106	40	52.43	7.59	13.16
				(52.81)	(7.70)	(13.19)
8	Blackish	105	30	55.25	7.51	12.53
	Chocolate			(55.33)	(7.20)	(12.32)
9	Blackish	85	35	63.34	7.21	12.49
	Chocolate			(63.30)	(7.39)	(12.65)
10	Yellow	125	30	51.73	11.09	12.79
	Chocolate			(51.34)	(11.23)	(12.82)

Table 2: Infrared spectral data for the prepared diazocoupled products

Products	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{N=N}$	ν_{C-N}	ν_{C-O}	$\nu_{Mo=O}$	ν_{Mo-O}
1	1670(vs)	1515(vs)	1415(vs)	1355(s)	1265(s)	915(s)	570(m)
2	1670(vs)	1515(vs)	1405(s)	1350(m)	1260(s)	960(m)	380(m)
						990(s)	390(m)
3	1670(vs)	1520(vs)	1370(s)	1300(s)	1265(s)	920(s)	560(m)
						960(s)	390(m)
4	1670(vs)	1500(vs)	1400(s)	1340(s)	1240(m)	920(s)	570(m)
							390(s)
5	1660(s)	1520(vs)	1420(s)	1360(s)	1260(s)	930(m)	570(m)
						990(m)	400(s)
6	1660(vs)	1490(s)	1400(m)	1340(m)	1250(s)	925(s)	560(s)
						980(m)	415(m)
7	1590(s)	1490(s)	1400(s)	1350(s)	1270(s)	900(s)	560(s)
						925(m)	410(s)
8	1635(s)	1490(vs)	1400(m)	1350(s)	1270(s)	900(s)	560(s)
						930(s)	410(s)
9	1590(s)	1500(ms)	1400(s)	1340(m)	1275(s)	900(s)	560(s)
						930(s)	410(s)
10	1630(s)	1480(s)	1400(m)	1345(s)	1280(m)	900(s)	555(s)
						925(s)	410(s)

Vs = very strong, s = strong, ms = medium strong and m = medium

Table 3: ¹HNMR spectral data for the prepared MoO₂(acac)₂ and diazocoupled products

Products	Signal	No. of proton	Group	Position δ
MoO ₂ (acac) ₂	Singlet	12H	CH ₃ -	2.3
	Singlet	2H	CH (methine)	5.4
2	Doublet	12H	CH ₃ -	2.3-2.56
	Multiplet	8H	Ph(asym)	7.0-7.5
3	Doublet	12H	CH ₃ -	2.37-2.68
	Doublet	12H	OCH ₃ -	3.7-4.0
6	Multiplet	6H	Ph (asym)	6.58-7.24
	Doublet	12H	CH ₃ -	2.3-2.53
	Multiplet	14H	Ph (asym)	7.24-7.84

remains about independent of the nature of the metal ion. A band near 1400 cm⁻¹ due to ν_{C-N} for copper (II) Schiff base complexes has been assigned^[21], whereas the band at 1441 cm⁻¹ of this vibration has been assigned^[22] for atetrahedral nickel (II) Schiff base complexes. The higher

frequency band at 1660-1720 cm⁻¹ was assigned^[23] due to $\nu_{C=O}$. The complex exhibit the band at 1230-1245 cm⁻¹ due to the ν_{C-O} (enolic) mode was also reported^[24].

β -diketonates exist as a mixture of ketonic and enolic forms in equilibrium with each other. A broad band in the bonded O-H region can detect the enolic form. For enolic form $\nu_{C=O}$ absorption band appears in the region 1580-1640 cm⁻¹ which much lower than that for conjugated ketones. This much lowering is due to the intra molecular hydrogen bonding established by resonance.

All β -diketonates absorbs in the ketonic form at near 1725 cm⁻¹. On coordination with metal in complexes, characteristic O-H band goes on absent due to deprotonation (enolic form) and the lowering of

Table 4: Electronic spectral data, magnetic moments and conductivity values for the prepared diazocoupled products

Products	Medium	Electronic spectral band (nm)	Magnet moment (B.M.)	Molar conductance (Λ_m , ohm ⁻¹ cm ² mol ⁻¹)
1	DMF	450, 368, 340, 268	Dia magnetic	3.90
2	DMF	450, 368, 268	Dia magnetic	4.90
3	DMF	410, 325, 269.5	Dia magnetic	4.50
4	DMF	535, 383, 291, 266	Dia magnetic	4.50
5	DMF	450, 368, 303, 267	Dia magnetic	4.90
6	DMF	408, 270.5	Dia magnetic	4.10
7	DMF	435, 310, 300	Dia magnetic	8.60
8	DMF	482, 314, 302	Dia magnetic	8.02
9	DMF	417, 302	Dia magnetic	7.30
10	DMF	384, 380, 292	Dia magnetic	8.11

DMF = Dimethyl formamate

absorption from 1725 to below 1700 cm⁻¹ are the evidences to the chelation of carbon group. In the present study of diazocoupled products of dioxomolybdenum (VI) chelates of β -diketonates, we report that the absence of any absorption at above 1670 cm⁻¹ indicate the carbonyl groups are involved in bonding with metal. The spectra of the compounds display in intense band at 1490-1520 cm⁻¹ and a medium intensity band at 1400-1420 cm⁻¹ which can be assigned to $\nu_{C=C}$ and $\nu_{C=N}$ respectively. The prepared diazocoupled products show the bands at 1260 cm⁻¹ for ν_{C-O} and 1340-1360 cm⁻¹ for ν_{C-N} bands. The bands at 400-560 cm⁻¹ are assigned to ν_{Mo-O} in our present studies.

MoO₂(aca)₂ was used for the substitution reaction with aryl diazonium ions. The substitution has occurred on both the chelate ring^[11] of MoO₂(aca)₂, is evident from the ¹HNMR spectrum of the diazocoupled products. Signals for methoxy protons of aryl azo part appear at δ 3.65^[25]. The ¹HNMR spectra of the presently prepared MoO₂(aca)₂ shows the methyl (12H) proton signal at δ 2.3 and methine (1H) proton signal at δ 5.4. The absence of methine proton signals in the diazocoupled products of MoO₂(acac)₂ indicate that the substitution has certainly occurred on both the chelate rings of MoO₂(acac)₂. The all diazocoupled products show a doublet signal for methyl proton at δ (2.3-2.7) in favour of enolic forms of β -diketonates^[25]. The same results were also found for the diazocoupled products of MoO₂(bzac)₂. The data obtained by ¹HNMR spectra clearly confirms the occurrence of diazocoupling reaction (Table 3).

Dioxomolybdenum (VI) complexes with dibasic tridentate ONO donor Schiff base ligands have been reported^[26] to exhibit three electronic absorption bands in DMF at 25975-25980 and 22200-23535 cm⁻¹ due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and the ligand to metal charge transfer, respectively. The electronic spectra, magnetic moment and the conductivity data of the prepared diazocoupled products are shown in Table 4. The band observed in the long wave length region may be attributed to the LMCT^[27]. The other high-energy bands are assigned to the intra ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The prepared diazocoupled products exhibit bands, which are in the range of 482-266.5 nm. In each case, the first low energy band is

assigned to the Ligand to Metal Charge Transfer (LMCT) transition. The other band have been assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intra ligand transition. No d-d transition is observed for the prepared diazocoupled products. Beyond 500 nm, there is no evidence of any d-d transition over the visible range. Electronic spectral bands of pure d-d transition were not expected in the presently prepared diazocoupled products having 4d⁰ configuration. The present diazocoupled products are, however colored only through their absorption's tailing inform the ultraviolet. In the present study, we did not feel it essential to determine the molar absorptivity of the prepared diazocoupled products because (i) no band in the visible region characteristic of d-d transition was observed which could have some charge transfer effect, (ii) the bands observed in the ultraviolet region are, as usual, very intense and (ii) the diazocoupled products were all experimentally found to be diamagnetic characteristic of the 4d⁰ molybdenum (VI) compounds.

The magnetic nature of the prepared diazocoupled products indicate 4d⁰ electronic configuration of the central molybdenum ion as expected for molybdenum (VI). Conductance studies shows that the prepared diazocoupled products are non-electrolytic nature.

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