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Iodination, Bromination and Isocyanation Reactions of β-Diketonates of Lanthanum(III), Cerium(IV), Thorium(IV) and Uranyl(VI)

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The reactions of coordinate ligands throw light on synthetic methodology to prepare macrocyclic molecules on the basis of template effect. This paper explains iodination, bromination, isocyanation reactions conducted on coordinated β-diketonates of lanthanum(III), cerium(IV) thorium(IV) and uranyl(VI).

Key Words: Reactivity-Phenylisocyanation prototropic rearrangement, Phenylamido substitutent, Lanthanum(III), Cerium(IV), Thorium(IV), Uranyl(VI).

INTRODUCTION

The reaction of coordinated ligands of transition metal ions are well studied[1,2]. Iodination, bromination, isocyanation and nitrosation reactions were conducted on coordinated β-ketonates/β-ketoiminates of Zn(II), Cd(II), Hg(II), Fe(III) and Co(III). Though several reactions on coordinated ligands are carried out on coordinated transition metal ions, reactions on coordinated lanthanides are meagre. Besides the isolation of a number of new complexes, sometimes involving noval methods of synthesis with varied applications have been suggested.

A general upsurge of interest in metal β-diketonates during last two decades[3] is also reflected in the chemistry of lanthanides. This has resulted in detailed investigation unfolding some lesser known facts of general lanthanide coordination chemistry. Early methods used for preparation of lanthanide *tris*-β-diketonates have been examined by Moeller *et al.*[4] who conclusively established that the products from aqueous solutions are invariably hydrates while sometimes hydroxy derivatives are also formed. Dutt and coworkers[5-8] prepared a large number of β-diketonates of lanthanides by Stites *et al.*[9] method.

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Literature survey does not give much report on the reactivity of β-diketonates of lanthanides. Hence to prove quasi aromatic property, iodination, bromination and isocyanation reactions were conducted on coordinated β-diketonates of lanthanum(III), cerium(IV), thorium(IV) and uranyl(VI).

EXPERIMENTAL

Cerium(IV) and thorium(IV) acetylacetonates were prepared by reported methods[10]. Lanthanum(III) acetylacetonate was prepared by a slight modification of the method of Sites *et al.*[9]. Uranyl-acetylacetonate was prepared according to the method of Comyns *et al.*[11].

Iodination reactions of cerium(IV), thorium(IV), lanthanum(III) and uranyl(VI) acetylacetonates: Solid monopyridineiodine(I) chloride (0.003 mol) was added to a solution of *tris*(acetylacetonate)lanthanum(III) (0.001 mol) in methanol (5.0 mL) and the resulting solution was stirred for 1 h under ice cold conditions. The complex was then finally recrystallized from methanol-acetone (1:1 by volume) mixture of $La(acacI)_3$.

The above procedure was repeated for the iodination of cerium(IV) acetylacetonate and thorium(IV) acetylacetonate by mixing M(IV) acetylacetonate (0.001 mol) and monopyridineiodine(I) chloride (0.004 mol).

In case of uranyl acetylacetonate, iodination was conducted by mixing uranyl acetylacetonate (0.001 mol) and monopyridineiodine(I) chloride (0.002 mol).

Phenylisocyanation reactions of La(III), Th(IV), Ce(IV), UO_2(VI) acetylacetonates: Phenylisocyanate (0.003 mol) was slowly added to a solution of *tris*(acetylacetonato) of La(III) (0.001 mol) in dry benzene. The reaction mixture was stirred using a magnetic stirrer in a flask equiped with reflux condenser carrying an anhydrous calcium chloride guard tube. The mixture was refluxed for 10 h till the precipitate was obtained. The precipitate was filtered, washed with benzene and dried in vacuum.

Phenylisocyanation of thorium(IV) and cerium(IV), were carried out by adding phenylisocyanate (0.004 mol) slowly to a solution of tetra *kis*(acetylacetonato)M(IV) (0.001 mol) [M(IV) = Ce(IV) and Th(IV)] in a dry benzene to get $Ce(acacC_6H_5NCO)_4$ and $Th(acacC_6H_5NCO)_4$.

In case of uranylacetylacetonate, phenylisocyanate (0.002 mol) was slowly added to a solution of $UO_2(acac)_2$ (0.001 mol) in dry benzene and the above procedure was followed. Finally, UO_2 $(acacC_6H_5NCO)_2$ was isolated as solid compounds.

Preparation of bromosubstituted β-diketonates of La(II), Ce(IV) and UO_2(VI): N-Bromosuccinimide (0.003 mol) was added to a solution of *tris*(acetylacetonato) La(0.001 mol) and the resulting solution was stirred for about 2 h. The precipitate obtained were collected by filtration and washed with ether. Finally the complex was recrystallized from methanol-acetone (1:1 v/v).

The above procedure is repeated for bromination of cerium(IV) acetylacetonate and thorium(IV) acetylacetonate by adding M(IV) acetylacetonate (0.001 mol) and N-bromosuccinimide (0.004 mol).

In the case of uranyl acetylacetonates bromination was conducted by adding uranyl acetonate (0.001 mol) to N-bromosuccinimide (0.002 mol) in dry benzene.

RESULTS AND DISCUSSION

Iodination reaction of the *bis*(acetylacetonato) of uranyl chelate using monopyridineiodine(I) chloride give diiodo derivatives whereas *tris* (acetylacetonato)La(III) give triiodo derivatives. *Tetrakis*(acetylacetonates) of Th(IV) and Ce(IV) give tetraiodo derivatives. All complexes are coloured crystalline solids stable under atmospheric condition and sparingly soluble in common organic solvents.

The reacted products of lanthanum(III) acetylacetonate, cerium(IV) acetylacetonate, thorium(IV) acetylacetonate and uranyl acetylacetonates are diamagnetic in nature.

The crystal and molecular structure of diaquo *tris*(acetylacetonato) lanthanum(III) was reported by Thedore Phillip *et al.*[12]. Each lanthanum ion is bonded to eight oxygen atoms, contributed by three bidentate acetylacetonate groups and two water molecules.

The average distance from a lanthanum ion to carbonyl oxygen atom is 2.473 Å while the average distance of lanthanum to coordinated water is 2.573 Å. The corresponding values[13] in $Y(C_5H_7O_2)_3{\cdot}3H_2O$ were 2.366 and 2.409 Å. The average O-O separation in a ring is 2.781 Å. This is comparable to the values of 2.80 Å found in $Y(C_5H_7O_2)_3{\cdot}3H_2O$ and 2.778 Å is the average of the 16 chelates surveyed by Lingafelter and Braun[14]. The coordination polyhedra formed by the eight oxygen atom about the lanthanum ion may be described as a distorted square antiprism[15].

The UV spectra of parent and substituted acetylacetonates of La(III) in $CHCl_3$, exhibits a peak around 275 mμ ($\varepsilon = 24{,}900$), $\lambda_{max} = 36400\ cm^{-1}$.

The parent $Ce(acac)_4$ and related $Ce(acac.I)_4$ and $Ce(acacC_6H_5NCO)_4$ are diamagnetic in nature. Analysis of the shape parameters for α-$Ce(CH_3CO\text{-}CHCOCH_3)_4$ indicate that the metal coordination polyhedra, most closely approximate C_2 bicapped trigonal prism.

Iodination reaction of *tris*(acetylacetonato)La(III) yielded *tris*-iodo substituted complex and *tetrakis*(acetylacetonato)M^{IV} ($M^{IV} = Ce^{IV}$ and Th^{IV}) yielded tetra iodo substituted complex. UO_2^{2+} ion acetylacetonato complexes yielded disubstituted iodo complexes. Similarly phenylisocynation reactions of *tris*(acetylacetonato)La(III) yields triphenylamido substituted complexes and *tetrakis*(acetylacetonato)M^{IV} ($M^{IV} = Ce^{IV}$ and Th^{IV}) yielded tetraphenylamido substituted complex. UO_2^{2+} ion acetylacetonato complexes yielded disubstituted phenylamido complexes.

Nature of bonding mode of bromo, iodo and phenylamido substituted complexes: The most complete band assignment of metal acetylacetonates have been based on normal coordinate treatment[16-19] and in some cases these assignments have been substantiated by studies of deuterium isotope shifts[18,19] and infrared dichroism. Raman spectra have been less extensively investigated, however Raman studies have been reported for a few acetylacetonate complexes[20,21]. Following the above findings (parent complex *tris*(acetylacetonato)La(III) exhibit the following characteristic frequencies (Table-1) around 627, 791, 1188, 1254, 1347, 1514 and 1634 cm^{-1} which are assignable to ν(M-O), δ(C-CH$_3$), π(CH), δ(CH), γ(C-C) and ν(CO) (coordinated), respectively[22].

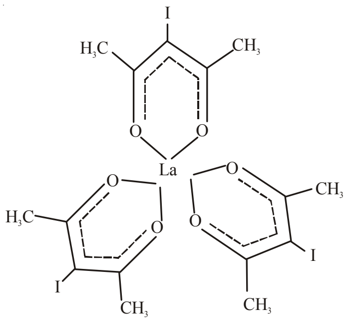
TABLE-1
IR FREQUENCIES FOR REACTED COMPLEXES

Complex	ν(CO) (coordinated)	π(CH)	δ(CH)	Amido	
				ν(CO)	ν(amido)
La(acac)$_3$	1634	785	1173	-	-
La(acacI)$_3$	1632	-	-	-	-
La(acacC$_6$H$_5$NCO)$_3$	1634	-	-	1689	3100-3500 m,b
Ce(acac)$_4$	1590	785	1173	-	-
Ce(acacI)$_4$	1606	-	-	-	-
Ce(acacC$_6$H$_5$NCO)$_4$	1605	-	-	1688	3110-3300 m,b
Th(acac)$_4$	1571	771	1187	-	-
Th(acacI)$_4$	1580	-	-	-	-
Th(acacC$_6$H$_5$NCO)$_4$	1571	-	-	1641	3100-3500 m,b
UO$_2$(acac)$_2$	1580	778	1200	-	-
UO$_2$(acacI)$_2$	1590	-	-	-	-
UO$_2$(acacC$_6$H$_5$NCO)$_2$	1522	-	-	1590	3100-3500 m,b

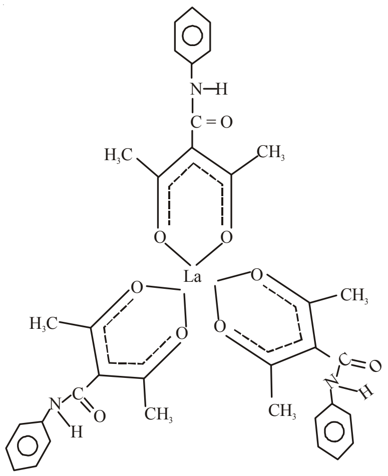
Iodinated *tris*(acetylacetonato)La(III), exhibits all the above frequencies except the frequencies assignable to π(CH) and δ(CH). Hence this findings exhibit the iodo substitution at all the three γ–CH position. PMR spectra also exhibit the absence of signals due to the methine proton. This is another evidence to show iodo substitution.

*Tris*phenylamido substituted *tris*(acetylacetonato)La(III) complex also shows the absence of bands due to π(CH) and δ(CH). New bands are found in the region around 1689 cm^{-1} and around 3400-3100 cm^{-1} (m, b) which are assignable to ν(CO)[amido] and ν(NH)[amido], respectively[23-25]. Hence this is clear that phenylisocyanate attacks at γ–CH and after prototropic rearrangement from phenylamido derivatives.

Based on the above spectral findings the following structures are assigned to iodo (structure **1**) and phenylamido substituted lanthanum chelates (structure **2**).



Structure **1**: La(acacI)$_3$



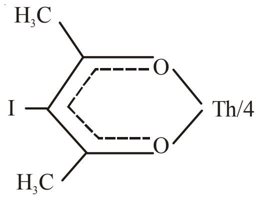
Structure **2**: La(acacC$_6$H$_5$NCO)$_3$

Nature of bonding mode of iodo and phenylamido substituted *terakis*(acetylacetonato)M^{IV} where M^{IV} = Ce^{IV}, Th^{IV}: Following the same type of argument as in parent complex *tetrakis*(acetylacetonato)Ce^{IV} and *tetrakis*(acetylacetonato)Th^{IV} exhibit characteristic IR frequencies around the region 680-647, 771-770, 1188-1187, 1267 and 1581-1571 cm^{-1} which are assignable to ν(M-O), δ(C-CH$_3$) or δ(ring), π(CH) and δ(CH) ν[S(C$\underline{---}$C] and ν(CO) (coordinated), respectively[14-22].

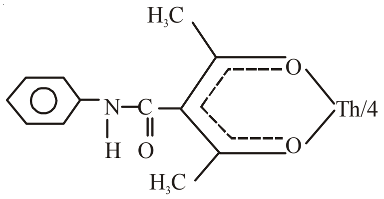
Following the earlier patterns of discussion the absence of π(CH) and δ(CH) (770 and 1187 cm^{-1}, respectively) can be taken to indicate that the parent complex has been totally substituted by the iodo and phenylisocyanate at the four γ-CH positions[23-25].

Further NMR spectra of tetraiodo substituted *tetrakis*(acetylacetonato) Ce(IV) and *tetrakis*(acetylacetonato)Th(IV) show the absence of characteristic NMR signals due to methine protons.

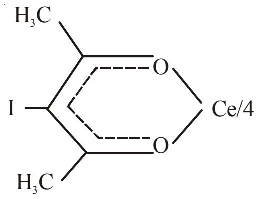
IR spectra of phenylamido substituted *tetrakis*(acetylacetonato)M(IV) [where M(IV) = Ce(IV) and Th(IV)] exhibit the absence of bands due to π(CH) and δ(CH) show new frequencies around 1650 and 3400-3100 cm^{-1} which are assignable to ν(CO)(amide), ν(NH)(amido), respectively[23-25].



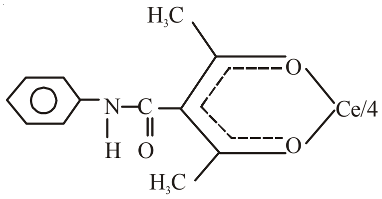
Structure **3**: Th(acacI)$_4$



Structure **4**: Th(acacC$_6$C$_5$NCO)$_4$



Structure **5**: $Ce(acac.I)_4$



Structure **6**: $Ce(acacC_6C_5NCO)_4$

Hence the parent complex have been totally substituted by the phenylisocyanate at the four γ-CH position with subsequent prototropic rearrangement to yield the *tetrakis* phenylamido substituted derivatives. Based on these data, the following structures may be proposed for iodo and phenylamido substituted complexes.

As normally prepared, uranyl acetylacetonate is obtained as the monohydrate $UO_2(acac)_2H_2O$ which is readily dehydrated to $UO_2(acac)_2$[26]. The IR spectra of uranyl complexes have been studied. But earlier studies were directed mainly to the problem of band assignments and conformation of the UO_2 group. A systematic study of the IR spectra of large range of uranyl β-diketonates was made in 1971 by Haigh and Thronton[26]. Theoretical and empirical evidence[27-29] unanimously support the assignment of the sharp intense band near 920 cm^{-1} in the spectra of the uranyl compounds to the symmetric uranyl stretching frequency ν(U=O). Correlation of group frequencies with the substitutent electronic effect requires some quantitative index. Use of Hammet parameter[30] (σ_m and σ_n) would assume aromaticity of the β-keto enolate ring. Although there is evidence of some electron delocalization in the chelate ring.

The metal ion provides a barrier to complete freedom of movement of the π-electron[31-33]. The first electronic effect of β-keto enolate substitutents is given by the equation.

$$\Sigma\sigma = f\,\Sigma\,F + \gamma\,\Sigma\,R$$

where f and γ are the relative weights of F and R.

The strongest band in the region 950-900 cm^{-1} in the spectra of the uranylacetylacetonate is assigned to the asymmetric stretching frequency of the uranyl ion. In other crystalline uranyl compound this vibration has been found[28] between 909 and 950 cm^{-1} typically near 920 cm^{-1}.

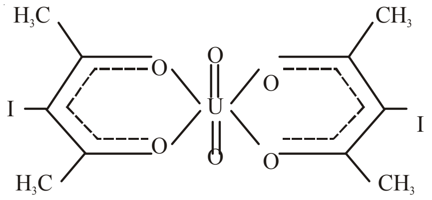
In the NMR spectra of iodinated uranylacetylacetonate the NMR signal characteristic of methine proton is absent indicating substitution (Table-2).

Further phenylamido substituted complex shows the absence of bands due to π(CH) and δ(CH). In addition to this, IR spectra of phenylamido substituted chelate exhibits the new characteristic frequencies around the region 1590 cm^{-1} and around 3800-3100 cm^{-1} (m, b) which are assignable

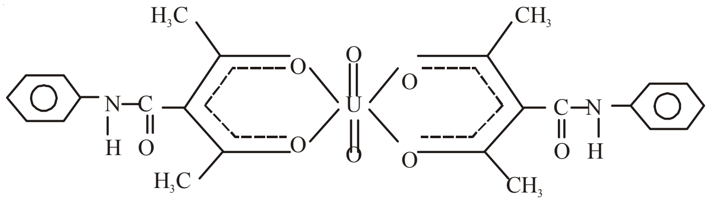
TABLE-2
NMR DATA OF URANYL ACETYL ACETONATE (δ ppm)

Compound	NMR Signal	
	γ(CH)	Amido NH
$UO_2(acac)_2$	6.4	-
$UO_2(acac)_2$	-	-
$UO_2(acac)(C_6H_5NCO)_2$	-	8.7

to ν(CO)(amido) and ν(CH)(amido), respectively[23-27]. Hence it is more probable that phenylisocyanate attacks on γ-CH proton and after prototropic rearrangement forms phenylamido substitutent.



Structure **7**: $UO_2(acac.I)_2$



Structure **8**: $UO_2(acacC_6H_5NCO)_2$

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