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β-Diketonate Ln^{3+} Chelates, Stereoisomerism and X-Ray Diffraction Studies of *Facial* Complexes Under Photochemical Condition

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Conversion, separation and characterisation of meridional isomer of series of *facial*—lanthanide (Br–β–diketonato/β–ketoester)$_3$ under photochemical condition is reported. When irradiated at $\lambda = 254$ nm, the *facial* stereoisomer—[Ln(Br–β–diketonato)$_3$·$2H_2O$] $2H_2O$ readily isomerises giving a product which has, on the basis of NMR and IR spectral details, been identified as the meridional isomer. The continuous photolysis on *facial*—[Ln(Br–β–ketoester)$_3$ ·$2H_2O$]$2H_2O$ readily hydrolyse which has, on the basis of X-ray diffraction data, been identified as $Ln(CH_3COO)_3 \cdot 4H_2O$. *Fac* → *Mer* stereiosomerism under thermal condition while met with failure.

INTRODUCTION

It was previously investigated[1], the conversion of $Ln(O,O')_3$ type tris-chelates into their linkage isomeric species $Ln(O, Br)_3$ from the halogenation under thermal condition, among other similar lanthanide (III)–β–diketonates[1–5]. On the basis of symmetry operations on constructed octahedral chelates[6] along with the literature[7,8], the complexes of the type $M(A-B)_3$ have two possible stereoisomers *viz. facial* and *meridional*. No attempt was made to convert the *facial* isomer without changing their substituents, which exist for *meridional* stereoisomer exclusively. Here, the investigation of *fac-mer* of [Ln (Br–β–diketonato/β–ketoester)$_3$·$2H_2O$]$2H_2O$ under thermal and photochemical conditions is reported.

EXPERIMENTAL

The *facial*– Ln(Br–β–diketonato)$_3$ and Ln(Br–β–ketoester)$_3$ were obtained by refluxing a solution mixture of the corresponding parent chelate (0.01 mol) and NBS (0.03 mol) in 5% DMF–$CHCl_3$ (150 cm^3) for 10 hrs. as described earlier[1].

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The solid product thus obtained was recrystallised from 50% H_2O–EtOH mixture. HPLC was performed using a MeOH–H_2O (1 : 4 v/v) solvent mixture for further purification until a 100% purity resulted.

Photolytic experiments were carried out in a reaction vessel connected to a vacuum line and a trap at room temperature. Solid products were isolated by vacuum distillation and subsequent evaporation of the solvent. The trap could be shut off and remove for product analysis in solution, was made by a Toshniwal Conductivity Bridge (Type CL. 01.02.A), Bausch and Lomb 160 UV-Vis spectrophotometer and by a HPLC analytical instrument.

In a typical reaction, a sample of HPLC pure *fac*-isomer by prolonged heating in aqueous ethanol (90%) for a period of 5–20 hrs., by reaction of excess NBS or by reaction with excess succinimide have been performed. The physical measurements of the solid products obtained were performed as reported earlier[1]. Three dimentional X-ray structure analysis was carried out on a ENRAF-Nonius CAD-4 diffractometer using Cu Kα. The single crystal analysis is performed by X-ray diffraction method using atomic scattering factors and a computor programme[9,10]

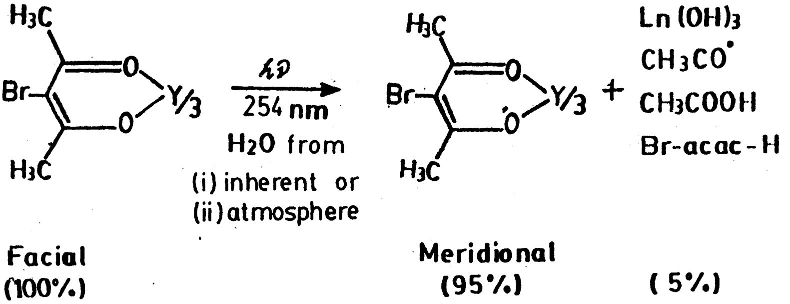
RESULTS AND DISCUSSION

The photochemical behaviour of β-ketoester chelates is drastically different from that of β-diketonates. Also the chemical composition of the product chelate is considerably differed from that of the substrate chelate.

Reactivity or β-dietonates

Preliminary analysis of the UV-illuminated (λ = 254 nm) substrate solution of β-diketonate, which has, on the basis of electronic spectral, conductivity and HPLC analytical data, been identified as CH_3CO, CH_3COOH, Br–β–diketone and Ln(Br–β–diketonate)$_3$ (SCHEME-1). The HPLC separated fraction yields a solid product upon evaporation which has identical chemical composition. *e.g.*, Y(Br–acac)$_3$·4H_2O ($YC_{15}H_{26}O_7Br_3$): Y = 12.58 (12.80), C = 25.84 (25.52), H = 3.70 (3.74) and Br = 34.60 (34.53)%.

SCHEME - I



The IR spectra of this solid product exhibit more number of bands in the IR and far IR regions. The frequencies corresponding to νC = O (free; 1720), and νC–O–M, (ring; 1200 cm^{-1}) in the substrate *facial* isomer appear as doublet or triplets in the product chelate.[1] And also in the far IR region (50–500 cm^{-1}) the product obtained after photolysis exhibit more number of bands than the substrate *facial* chelate (Figure-1). The bands appear at 182 cm^{-1} and 412 cm^{-1} corresponding to Ln–O and Ln–Br[2,11] respectively in the substrate *facial* chelate. These bands also split into three bands upon irradiation. These IR and far IR features are characteristic for a loss in symmetry. It has been therefore suggested that the C_3–symmetric substrate could isomerise to a species which we believe to contain the three ligands in the *meridional* geometry.

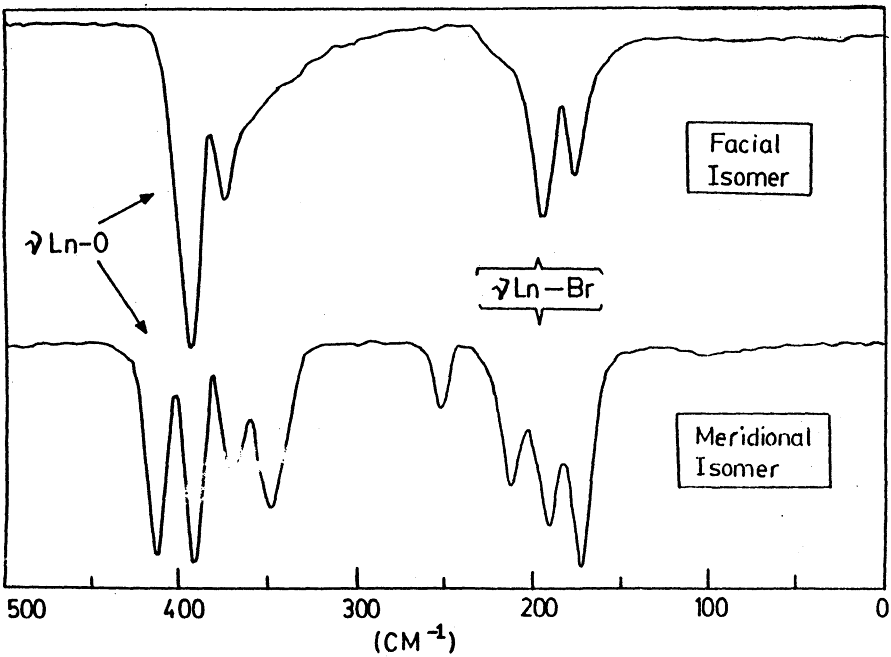


Fig. 1. Far-IR spectra of *facial* and *meridional* steroisomers. Frequency around at 400 cm^{-1} correspond to νLn-O and around at 190 cm^{-1} correspond to νLn-Br

In light of the contrast in geometries between the *facial* and *meridional* isomers of a tris-octahedral chelate, NMR studies are ideal for the distinction of such isomers[1,12,13]. An examination of the ^1H NMR spectra as shown in Figure–2, in the photolytic product exhibit three-line-signal pattern of near equal intensity as against single-line signals for the methyl groups of the substrate, are observed. As expected the proton-noise decoupled ^{13}C NMR spectra also resolved three-line-signal pattern (Figure-3) for all the chemically different carbon atoms for the product chelate.

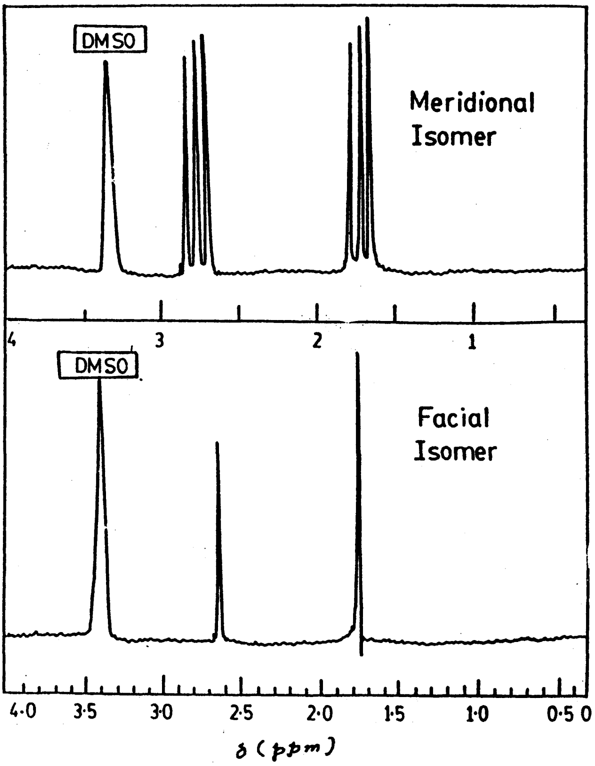
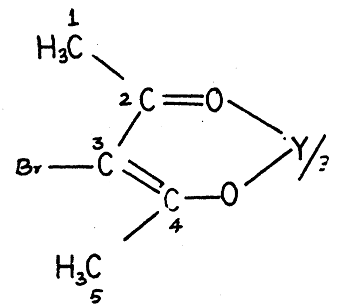


Fig. 2. ^{1}H NMR spectra of *facial* (bottom) and *meridional* (top) stereoisomers, showing 3 line-signal pattern.

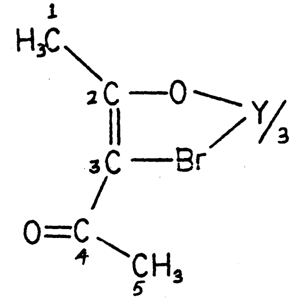
TABLE 1
^{1}H NMR DATA OF THE REPRESENTATIVE TRIS (β-DIKETONATO) YTTRIUM (III) COMPLEXES.

No.	Compound	Type	Symmetry	CH_3 1	CH 3	CH_3 5
1	$Y(H\text{-}acac)_3$	Parent	C_3	1.87	5.3	1.87
2	$Y(Br\text{-}acac)_3$	Unflipped	C_3	1.93	—	1.93
3	$Y(Br\text{-}acac)_3$	Rearranged Facial	C_3	1.79	—	2.65
4	$Y(Br\text{-}acac)_3$	Rearranged Meridional	C_1	1.66 1.79 1.87	—	2.67 2.75 2.89

All spectra were run in CD_3SOCD_3 with the exception of the parent which was run in CD_3COCD_3.



Six membered chelate ring
M(A–A)3 type chelate



Five membered chelate ring
M(A–B)3 type chelate

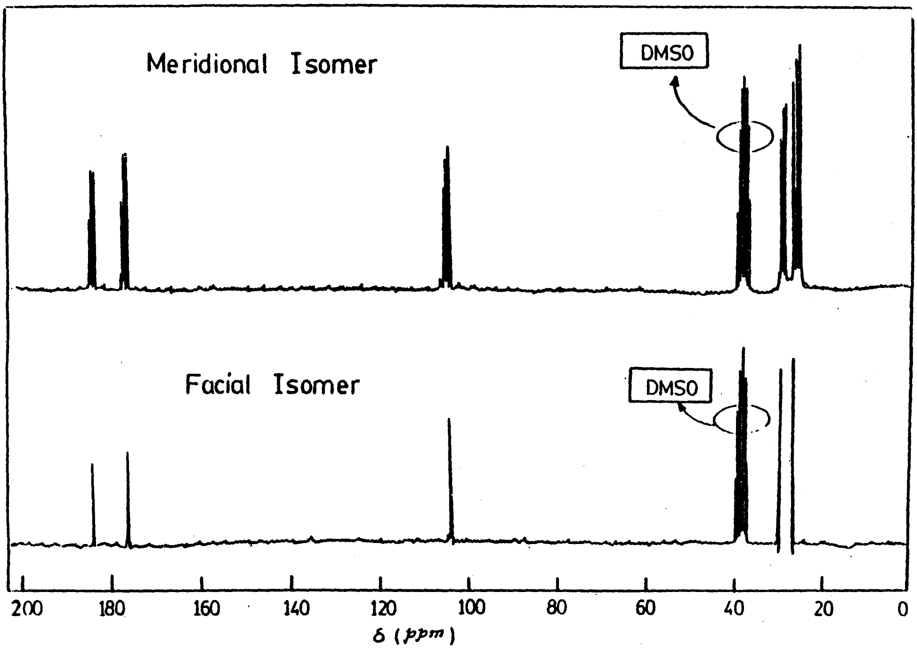


Fig. 3. ^{13}C NMR spectra of *facial* (bottom) and *meridional* (top) steroisomers showing three-line-signal pattern.

The X-ray analysis on the triclinic crystal of the product chelate suggest that the β- diketonates undergo chemical degradation against X-rays. In line with the above arguements, in conjunction with the symmetry operations on a similar tris-chelated octahedral model one developed by Ramalingam et al.,[6] it should be concluded that the *fac*-β- diketonate ligands could morphologically be changed into *meridional* geometry up on photolysis.

Photochemical Behaviour of β-Ketoester Chelates

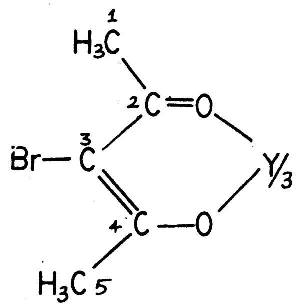
Evaporation of the photolysed solution yields triclinic crystals of dimensions

TABLE 2

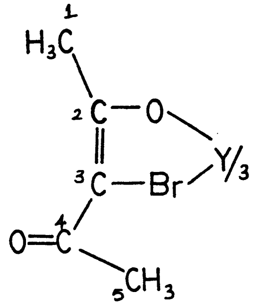
^{13}C NMR DATA OF THE REPRESENTATIVE TRIS (β-DIKETONATO) YTTRIUM(III) COMPLEXES

No.		CH_3 1	C=O 2	C–X 3	C=O 4	CH_3 5
1	Parent unsubstituted	27.16	188.52	100.72	188.52	27.16
2	Unflipped -Brominated	25.63	175.55	185.62 (X = Br)	175.55	25.63
3	Rearranged -brominated *(facial)*	29.72	100.74	186.07 (X = Br)	178.69	29.91
4	Rearranged -brominated *(meridional)*	28.43 29.32 29.98	101.18 100.46 99.90	186.81 186.21 185.42 (X = Br)	178.82 178.21 177.43	30.25 30.96 31.44

All spectra were run in CD_3SOCD_3 with the exception of the parent which was run in CD_3COCD_3.



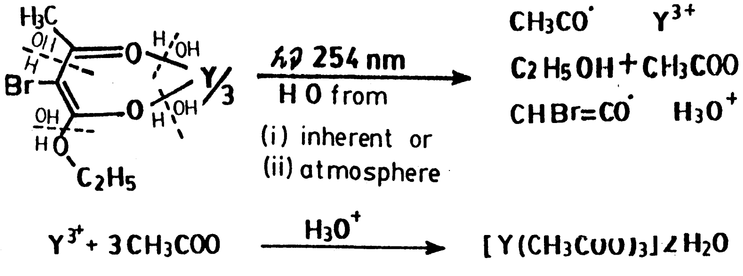
Six membered chelate ring
M(A–A) type chelate



Five membered chelate ring
M(A–B) type chelate

ranging from 0.20 to 0.30 mm^3. These crystals are stable against X-rays. The crystals data are given in Table-3, and the bond angles given in Table-4. The bond lengths and numbering scheme are given in Figure-4 as well as in Table-5. From these data it is suggested that a dimeric or polymeric unit for the compound involving a H-bonding network (due to H_2O molecules) around the central metal atoms. The mechanistic pathway for the β-ketoester chelates upon photolysis is given as below (SCHEME-II).

SCHEME-II



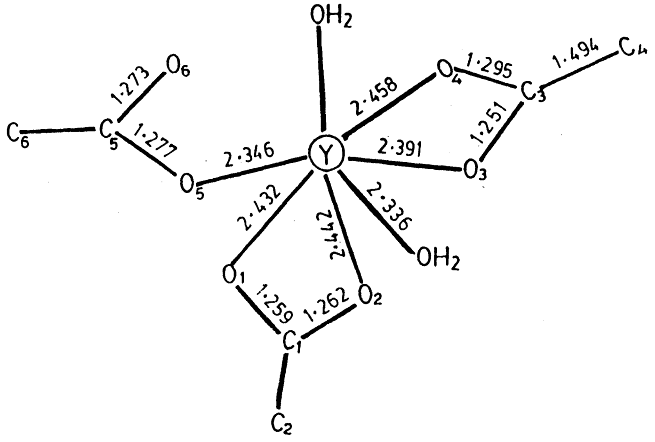


Fig. 4. Bond distances and numbering arrangement of $Y(CH_3COO)_3 \cdot 4H_2O$

TABLE 3

CRYSTAL DATA FOR THE $[Y(CH_3COO)_3 \cdot 2H_2O]2H_2O$

Crystal dimensions = 0.20 × 0.15 × 0.30 mm^3

Total No of Reflection = 2247

a = 8.800 (3) Å

b = 9.244 (3) Å

c = 10.571 (4) Å

α = 65.10 (3)

β = 64.26 (3)

γ = 62.12 (3)

Volume of the Unit Cell = 663.5 θ^3

Formula weight = 336.92

Observed density = 1.686 gms/cc

No of molecules in the unit cell = 2

Mo K radiation space group = $P\bar{1}$

Crystal system = triclinic

Number of electrons in the unit cell F(OOO) = 350

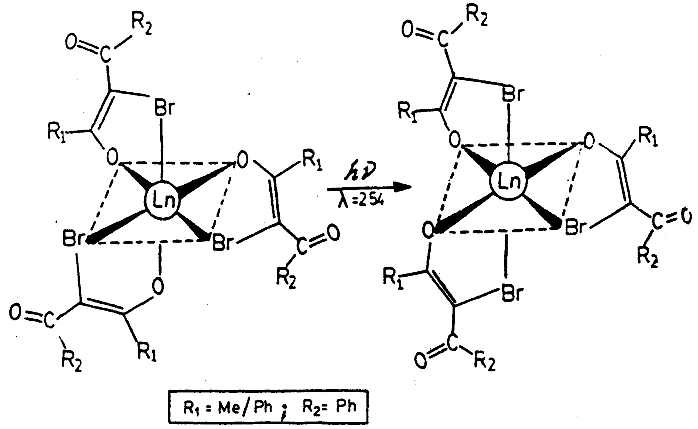


TABLE 4
BOND ANGLES BETWEEN THE NON-HYDROGEN ATOMS OF [Y(acetate)$_3$·2H$_2$O]2H$_2$O

O_1—Y—O_2	53.13°
O_1—Y—O_3	78.70°
O_1—Y—O_5	77.06°
O_2—Y—O_3	73.30°
O_2—Y—O_5	78.90°
O_3—Y—O_4	53.60°
OH_2—Y—O_2	73.80°
OH_2—Y—O_4	77.70°
OH_2—Y—O_5	78.00°
OH_2—Y—OH_2	78.50°

TABLE 5
BOND LENGTHS (Å) BETWEEN THE NON-HYDROGEN ATOMS OF [Y(CH$_3$·COO)$_3$·2H$_2$O]2H$_2$O

O_1—C_1	1.259;	O_1—Y	2.442
O_2—C_1	1.262;	O_2—Y	2.442
O_3—C_3	1.251;	O_3—Y	2.391
O_4—C_3	1.295;	O_4—Y	2.458
O_5—C_5	1.277;	O_5—Y	2.346
O_6—C_5	1.273;	O_6—Y	—
C_1—C_2 C_3—C_4 C_5—C_6	1.494;	Y—OH_2	2.336

Finally it should be concluded here that the *fac-mer* stereoisomerism in β-diketonates and a chemical degradation in β-ketoester chelates instead of photoresolution might be explained by the following factors:

(i) the tris (β-diketone/β-ketoester) chelate rings are facile to ring rearrangement.[1].
(ii) the capability of having coordination number for Ln^{3+} ranging from 6 to 12.
(iii) the hydrolysing capability of Ln^{3+} is high ($pK_4 = 11.5$)[14] and
(iv) the differential behaviour of the β-ketoester chelates may be explained by the fact that they hydrolyse before Ln^{3+} can hydralyse appreciably.

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