

Secondary Amide Derivatives of Lanthanons

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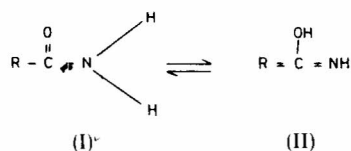
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Reactions of lanthanon isopropoxides (Pr, Nd, Sm, Dy & Ho) with N-(4-bromophenyl)-, N-(2-ethoxyphenyl)-, N-(4-ethoxyphenyl)-, N-(2-tolyl)-, N-(4-tolyl)- and N-(2-pyridyl)-acetamides and N-(2-tolyl)- and N-(4-tolyl)-benzamides have been carried out in dry benzene. Products of the type $\text{Ln}(\text{OPr}^i)_2\text{L}$, $\text{Ln}(\text{OPr}^i)_2\text{L}_2$ and LnL_3 (where L is the deprotonated secondary amide) are obtained. All these compounds are microcrystalline solids and soluble in benzene. The compounds have been characterized by means of chemical analyses and IR spectral data.

Transition metal complexes with primary and secondary amides have been widely investigated¹⁻³. Gray and coworkers⁴ have prepared the complexes of Co(II) and Ni(II) perchlorates with 4-substituted acetanilides. A survey of literature reveals that though some work has been carried out on the adducts of lanthanons with amides^{5,6}, only a few references are available on the adducts of lanthanons with secondary amides⁷, and no work has been reported on the substituted derivatives of lanthanons. We report here for the first time a series of new lanthanon complexes derived from an anionic amide.

It has been established that the protonation of amides takes place at the carbonyl oxygen. There appears, therefore, that in N-substituted amides, a state of tautomeric equilibrium exists between the two forms (I) and (II):



and it is the enolic form(II) which reacts with lanthanon isopropoxide to give substitution products. The present note deals with the preparation and properties of lanthanon derivatives derived from the reaction between lanthanon isopropoxide and the secondary amides, viz., N-(4-bromophenyl)-, N-(2-ethoxyphenyl)-, N-(4-ethoxyphenyl)-, N-(2-tolyl)-, N-(4-tolyl)-, and N-(2-pyridyl)-acetamides and N-(2-tolyl)- and N-(4-tolyl)-benzamides.

The experiments were performed in all glass apparatus taking precaution to exclude moisture.

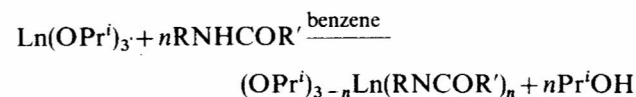
Benzene (BDH. AR) was kept over sodium wire (3-4 days) and finally distilled. Lanthanon isopropoxides

were prepared by sodium alkoxide method⁸. N-(4-bromophenyl)-, N-(2-ethoxyphenyl)-, N-(4-ethoxyphenyl)-, N-(2-tolyl)-, N-(4-tolyl)-, N-(2-pyridyl)-acetamides and N-(2-tolyl)- and N-(4-tolyl)-benzamides were recrystallised from ethanol and dried *in vacuo* before use.

The complexes were prepared by the addition of different stoichiometric amounts of a lanthanon isopropoxide and the respective anilide in anhydrous benzene (~ 65 ml) and refluxing over a fractionating column. The isopropanol liberated during the course of above reaction was collected azeotropically with benzene. The progress of the reaction was ascertained by the estimation of isopropanol in the azeotrope⁹. The products were rendered free from solvent by distillation *in vacuo* and finally dried at room temperature *in vacuo* for 3-4 hr.

The lanthanides in the complexes were estimated as the oxides, M_2O_3 , by first precipitating them as oxalates. Nitrogen was estimated by Kjeldahl's method. Bromine was estimated gravimetrically as silver bromide. Isopropanol in the azeotrope was estimated by oxidation with 1.0 N dichromate solution in 12.5% sulphuric acid⁹. Infrared spectra were recorded in KBr on a Perkin Elmer 577 spectrophotometer.

The reactions between lanthanon isopropoxide and N-(4-bromophenyl)-, N-(2-ethoxyphenyl)-, N-(4-ethoxyphenyl)-, N-(2-tolyl)-, N-(4-tolyl)-, N-(2-pyridyl)-acetamides and N-(2-tolyl)- and N-(4-tolyl)-benzamides in refluxing benzene in different stoichiometric ratios yielded products of the type $\text{Ln}(\text{OPr}^i)_{3-n}\text{Ln}$; where L = deprotonated secondary amide, Ln = Pr, Nd, Sm, Dy and Ho and n = 1, 2 or 3. These reactions can be represented by the following general equation:



All these reactions were endothermic and facile as expected and the products were obtained in almost quantitative yields (90-97%). The replacement of one or two isopropoxy groups by the ligand molecules was easy but further replacement needed prolonged refluxing. The longer time needed for completion of such reactions could be due to steric hindrance¹⁰. These reactions are summarised in Tables 1-4.

These compounds have colours characteristic of the trivalent state of the corresponding lanthanon ion. Mono- and di-substituted anilide derivatives were

Table 1—Synthesis and Analytical Data of Complexes of Lanthanon(III) with Amides of the Type RNHCOBr

Complex* (colour)	Found(Calc.), %			m.p. (°C)
	Metal	N	Br	
Pr(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) (Green)	24.67 (24.77)	2.46 (2.46)	13.97 (14.05)	190(d)
Pr(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) ₂ (Green)	22.74 (22.74)	4.32 (4.46)	24.81 (25.50)	150-52
Pr(C ₆ H ₄ NCOCH ₃ Br) ₃ (Green)	18.00 (18.05)	5.30 (5.38)	30.49 (30.75)	144-46
Nd(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) (Violet)	25.86 (25.21)	2.82 (2.44)	19.46 (19.96)	205(d)
Nd(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) ₂ (Violet)	22.98 (22.90)	4.61 (4.44)	24.83 (25.37)	165
Nd(C ₆ H ₄ NCOCH ₃ Br) ₃ (Violet)	18.07 (18.42)	5.04 (5.35)	29.89 (30.63)	148
Sm(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) (Light-Yellow)	28.17 (28.80)	2.49 (2.66)	15.07 (15.24)	260(d)
Sm(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) ₂ (Light-Yellow)	23.95 (23.70)	4.31 (4.39)	24.99 (24.98)	145-47
Sm(C ₆ H ₄ NCOCH ₃ Br) ₃ (Light-Yellow)	19.34 (19.11)	5.34 (5.30)	30.09 (30.36)	154.56
Dy(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) (White)	30.35 (30.35)	2.19 (2.61)	14.87 (14.89)	290(d)
Dy(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) ₂ (White)	25.06 (25.07)	4.61 (4.31)	25.37 (24.60)	150-52
Dy(C ₆ H ₄ NCOCH ₃ Br) ₃ (White)	20.35 (20.29)	4.98 (5.24)	30.19 (29.92)	158-60
Ho(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) (Cream)	30.09 (30.66)	2.40 (2.60)	15.00 (14.86)	210(d)
Ho(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ Br) ₂ (Cream)	25.90 (25.34)	4.46 (4.29)	25.12 (24.56)	155-56
Ho(C ₆ H ₄ NCOCH ₃ Br) ₃ (Cream)	20.48 (20.52)	5.12 (5.22)	28.07 (29.84)	163-67

* Yield ~95%; crystalline compounds soluble in benzene, DMSO and DMF

Table 2—Synthesis and Analytical Data of Complexes of Lanthanon(III) with Amides of the type RNHCOCH₃OC₂H₅

Complex* (colour)	Found(Calc.), %		m.p. (°C)
	Metal	N	
Pr(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) (Green)	32.00 (32.07)	3.11 (3.18)	220(d)
Pr(OPr ⁱ)(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₂ (Green)	24.90 (24.86)	4.41 (4.94)	145(d)
Pr(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₃ (Light-Green)	20.84 (20.84)	6.01 (6.20)	110(d)
Nd(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) (Violet)	32.68 (32.60)	3.13 (3.16)	210(d)
Nd(OPr ⁱ)(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₂ (Violet)	25.45 (25.37)	4.92 (4.90)	180(d)
Nd(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₃ (Violet)	21.55 (21.29)	6.47 (6.18)	120(d)
Sm(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) (Yellow)	33.11 (33.63)	3.09 (3.11)	140(d)
Sm(OPr ⁱ)(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₂ (Yellow)	26.10 (26.18)	4.55 (4.85)	130(d)
Sm(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₃ (Yellow)	22.31 (22.07)	6.27 (6.12)	100(d)
Dy(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) (White)	35.71 (35.28)	3.70 (3.03)	230(d)
Dy(OPr ⁱ)(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₂ (White)	27.80 (27.64)	4.42 (4.75)	210(d)
Dy(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₃ (White)	23.36 (23.31)	5.98 (6.01)	200(d)
Ho(OPr ⁱ) ₂ (C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) (Cream)	35.62 (35.60)	3.20 (3.02)	240(d)
Ho(OPr ⁱ)(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₂ (Cream)	28.01 (27.93)	4.09 (4.74)	60(d)
Ho(C ₆ H ₄ NCOCH ₃ OC ₂ H ₅) ₃ (Cream)	23.23 (23.52)	5.55 (5.99)	195(d)

* Yield ~95-98%; crystalline solids, soluble in benzene, DMSO and DMF

susceptible to hydrolysis. Most of these derivatives had sharp melting points with the exception of a few which did not melt completely, and heating to still higher temperature led to their decomposition ($\sim 300^\circ\text{C}/0.5\text{ mm}$). The substituted amides having a hetero ring were found to be more reactive as compared to the other aromatic substituted amides.

The IR band assignments in the spectra of the present complexes are based on the infrared studies of the substituted amides^{11,12}.

Free anilides show a strong band around 3270 cm^{-1} which is assigned to νNH . The position of the band depends on the degree of hydrogen bonding in these substituted amides as well as the substituents present in the aromatic ring. The intensity of the νNH mode in secondary amides is rather insensitive to polar effects¹³. This band is absent in all the substituted amide derivatives of lanthanons showing deprotonation of the N-H group. The $\nu\text{C}=\text{O}$ band in the spectra of secondary amide appears near 1670 cm^{-1}

(known as amide-I^{11,12} band), and another band between 1650 and 1515 cm^{-1} (known as amide-II band) is due largely to $\delta\text{N-H}$ mode. Both these bands are influenced by the size of the ring and the substituent groups.

The $\nu\text{C}=\text{O}$ band in the derivatives shifts to slightly lower wave numbers, compared to the corresponding $\nu\text{C}=\text{O}$ vibration in free anilides indicating involvement of the oxygen atom in coordination.

The amide-II band ($\delta\text{NH} + \nu\text{C}-\text{N}$) appears as a weak band at $\sim 1550\text{ cm}^{-1}$ in lanthanon derivatives, possibly due to $\nu\text{C}-\text{N}$ only, showing the absence of NH group in the complexes. The amide-III band ($\nu\text{C}-\text{N}$ mode which is usually observed at $\sim 1300\text{ cm}^{-1}$) is observed at slightly higher wave numbers in lanthanon derivatives.

Mono- and di-isopropoxy derivatives of secondary amides show characteristic absorption of the isopropoxy group at 1170 , 1145 , 1135 , $960-945$ and $820-750\text{ cm}^{-1}$. The strong band in the region $1010-$

Table 3—Synthesis and Analytical Data of Complexes of Lanthanon(II) with Amides of the Type $C_5H_4-NHCOCH_3$

Complex* (colour)	Found(Calc.), %		m.p. (°C)
	Metal	N	
Pr(OPr ⁱ) ₂ C ₇ H ₇ N ₂ O (Light-green)	35.30 (35.52)	7.00 (7.08)	195(d)
Pr(OPr ⁱ)(C ₇ H ₇ N ₂ O) ₂ (Light-green)	29.77 (29.85)	11.82 (11.91)	160-62
Pr(C ₇ H ₇ N ₂ O) ₃ (Light-green)	25.70 (25.78)	15.36 (15.40)	124-26
Nd(OPr ⁱ) ₂ C ₇ H ₇ N ₂ O (Pink)	35.41 (36.13)	6.98 (7.01)	180(d)
Nd(OPr ⁱ)(C ₇ H ₇ N ₂ O) ₂ (Pink)	30.97 (30.41)	11.79 (11.81)	135-38
Nd(C ₇ H ₇ N ₂ O) ₃ (Pink)	27.46 (26.25)	15.50 (15.30)	98-100
Sm(OPr ⁱ) ₂ (C ₇ H ₇ N ₂ O) (Yellow)	37.87 (37.17)	6.75 (6.89)	200(d)
Sm(OPr ⁱ)(C ₇ H ₇ N ₂ O) ₂ (Yellow)	31.38 (31.38)	11.55 (11.65)	140-42
Sm(C ₇ H ₇ N ₂ O) ₃ (Light-yellow)	27.21 (27.13)	15.04 (15.11)	100-102
Dy(OPr ⁱ) ₂ (C ₇ H ₇ N ₂ O) (White)	39.09 (38.98)	6.38 (6.70)	175(d)
Dy(OPr ⁱ)(C ₇ H ₇ N ₂ O) ₂ (White)	33.05 (33.05)	11.47 (11.36)	148-50
Dy(C ₇ H ₇ N ₂ O) ₃ (White)	28.51 (28.68)	14.79 (14.79)	105-08
Ho(OPr ⁱ) ₂ (C ₇ H ₇ N ₂ O) (Cream)	40.00 (39.27)	6.43 (6.67)	160(d)
Ho(OPr ⁱ)(C ₇ H ₇ N ₂ O) ₂ (Cream)	33.61 (33.33)	11.27 (11.32)	158-60
Ho(C ₇ H ₇ N ₂ O) ₃ (Cream)	29.12 (28.94)	14.35 (14.74)	142-44

* Yield ~95%; crystalline solids, soluble in benzene, DMSO and DMF

Table 4—Synthesis & Analytical Data of Complexes of Lanthanons(III) with Amides of the Type R(CH₃)NHCOR

Complex* (colour)	Found(Calc.), %		m.p. (°C)
	Metal	N	
Pr(OPr ⁱ) ₂ (C ₆ H ₄ NCOC ₆ H ₅ CH ₃) (Light-brown)	30.04 (30.05)	2.79 (2.96)	> 360
Pr(OPr ⁱ)(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₂ (Light-brown)	22.90 (22.77)	4.35 (4.52)	100
Pr(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₃ (Dirty-white)	18.57 (18.57)	5.40 (5.53)	124-28
Nd(OPr ⁱ) ₂ (C ₆ H ₄ NCOC ₆ H ₅ CH ₃) (Light-brown)	31.33 (30.54)	2.85 (2.96)	> 360
Nd(OPr ⁱ)(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₂ (Brown)	23.20 (23.18)	4.01 (4.50)	174-76
Nd(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₃ (Brown)	19.05 (18.92)	5.42 (5.50)	110-15
Sm(OPr ⁱ) ₂ (C ₆ H ₄ NCOC ₆ H ₅ CH ₃) (Brown)	30.99 (31.43)	3.07 (2.92)	> 360
Sm(OPr ⁱ)(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₂ (Brown)	23.91 (24.00)	4.51 (4.45)	165-68
Sm(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₃ (Brown)	20.03 (20.53)	5.58 (5.46)	180
Dy(OPr ⁱ) ₂ (C ₆ H ₄ NCOC ₆ H ₅ CH ₃) (Light-brown)	33.90 (33.11)	2.50 (2.84)	> 360
Dy(OPr ⁱ)(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₂ (Light-brown)	25.81 (25.42)	4.30 (4.37)	140-45
Dy(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₃ (Light-brown)	20.98 (20.37)	5.00 (5.29)	110-12
Ho(OPr ⁱ) ₂ (C ₆ H ₄ NCOC ₆ H ₅ CH ₃) (Pink)	33.42 (33.39)	2.85 (2.83)	> 360
Ho(OPr ⁱ)(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₂ (Pink)	26.11 (25.65)	4.30 (4.35)	110-12
Ho(C ₆ H ₄ NCOC ₆ H ₅ CH ₃) ₃ (Light-pink)	20.62 (20.62)	5.20 (5.27)	115-18

* Yield ~90%; crystalline solids, soluble in benzene, DMSO & DMF

1000 cm⁻¹ in these derivatives can be assigned to the ν C—O mode found at 1070 cm⁻¹ in 2-propanol¹⁴. The value of the ν C—O vibration at ~1010 cm⁻¹ agrees with the ν C—O vibration of the bridging isopropoxide group¹⁵; the bridging nature is further supported by the presence of bands at 930 and 800 cm⁻¹ in isopropoxy derivatives.

Secondary amide derivatives of lanthanon show two weak bands in the region 300-200 cm⁻¹ which have been assigned to M-N (ligand) vibrations¹⁶. Finally, the spectra of these derivatives are not significantly different from each other, except for bands due to different substituents.

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