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β-Diketonates of a Few Lanthanide Elements

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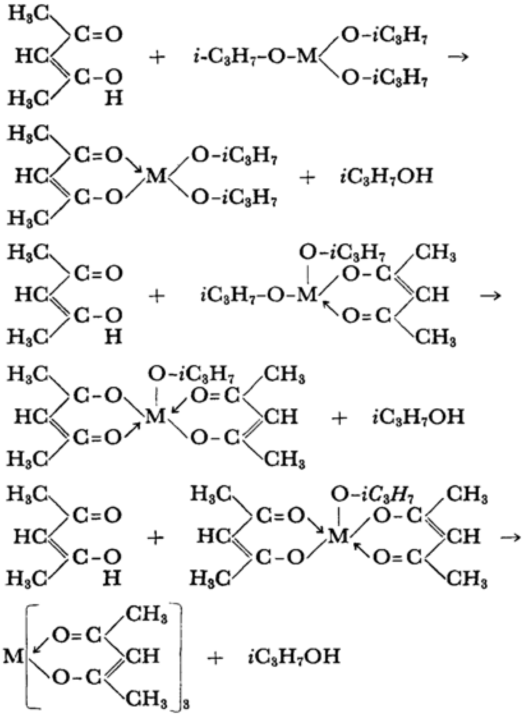
The reactions of isopropoxide of praseodymium and neodymium with benzoylacetone, dibenzoylmethane have been studied and the derivatives of the type $M(O\text{–}iPr)_2(\text{lig.})$, $M(O\text{–}iPr)(\text{lig.})_2$ and $M(\text{lig.})_3$ (where lig.=benzoylacetone or dibenzoylmethane) have been isolated. The isopropoxide-diketonates on treatment with tertiary butanol interchange their isopropoxide group with tertiary butoxide group. Anhydrous acetylacetonates of lanthanum, praseodymium, neodymium and samarium have been prepared from the reactions of the alcoholic solution of the chlorides with alcoholic solution of ammonium acetylacetonates. The molecular weights of these β-diketonates and alkoxides β-diketonates have been measured ebullioscopically in boiling benzene.

In recent years there has been considerable interest in the preparation and properties of metal acetylacetonate derivatives. An extensive study of literature reveals that an appreciable amount of work has been done on the acetylacetonates of lanthanide elements.[1-9]

In almost all the methods, the reactions were carried out in an aqueous medium (hydrated organic solvents were also employed), by taking hydrated metal chloride and the mono- and trihydrated acetylacetonates were isolated.

Recently the anhydrous acetylacetonates and alkoxide acetylacetonates of praseodymium and neodymium[10] have been synthesised from the reactions of their isopropoxides with acetylacetone in different stoichiometric ratios in benzene: The raction mechanism appears most probably of S_N2 type:



In view of the above, it was considered of interest to study the reactions of praseodymium and neodymium isopropoxides with benzoylacetone and dibenzoylmethane in benzene.

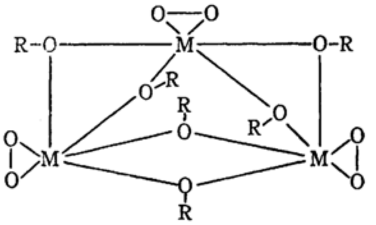
All these derivatives are coloured microcrystalline solids, soluble in benzene and ethanol from which the pure samples could be crystallised.

The alkoxide β-diketonates interchange their isopropoxide group with tertiary butoxide group, when refluxed with tertiary butanol in benzene, isopropanol produced in the reaction was fractionated out azeotropically with benzene:

$$M(O\text{-}iC_3H_7)_2L + 2tC_4H_9OH$$
$$= M(\text{-}O\text{-}tC_4H_9)_2L + 2iC_3H_7OH$$
$$M(O\text{-}iC_3H_7)L_2 + tC_4H_9OH$$
$$= M(\text{-}O\text{-}tC_4H_9)L_2 + iC_3H_7OH$$

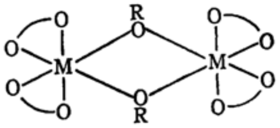
The synthesis of anhydrous acetylacetonates of lanthanum, praseodymium, neodymium and samarium has been followed by another route. Ammonium acetylacetonate (prepared by passing a controlled slow current of ammonia through the solution of acetylacetone in benzene when a crystalline solid separated out; it was filtered) was dissolved in ethanol and this solution was added to the alcoholic solution of metal chloride, when a white precipitate of ammonium chloride separated out leaving clear liquor. The product was obtained after evaporating off the solvent under reduced pressure. The product was recrystallized from refluxing benzene and thus could be obtained in a high grade of purity.

The molecular weight determination of the di-isopropoxide monoligand derivative showed that the molecule is a trimer and thus can be represented-most probably by the following structure:



Where we have three metal octahedra with two edges in common. In this structure the coordination number of the metal appears to be six.

The mono alkoxide diligand derivative has been found to be dimeric and thus can be represented by the following structure:



Where two metal octahedra are bridged through alkoxide oxygen bridges.

The triligand derivative has been found to be dimeric and thus the following structure appear to be a probable one:

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1) G. Janstch and E. Meyer, *Ber.*, **53B**, 1577 (1920).

2) S. Freed, S. I. Weissman and F. E. Fortess, *J. Am. Chem. Soc.*, **63**, 1079 (1941).

3) J. K. Marsh, *J. Chem. Soc.*, **1947**, 1084.

4) J. G. Stites, C. N. Mc. Carty and L. L. Quill, *J. Am. Chem. Soc.*, **70**, 3140 (1949).

5) T. Moeller and W. F. Ulrich, *J. Inorg. Nucl. Chem.*, **2**, 164 (1956).

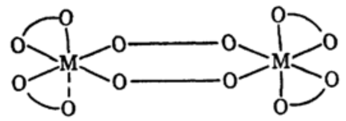
6) N. K. Dutt and P. Bandyopadhyay, *Science and Culture*, **23**, 105 (1957); **23**, 690 (1957); **23**, 365 (1957); **24**, 38 (1958); **27**, 403 (1961).

7) J. F. Steinbach and J. H. Burne, *J. Am. Chem. Soc.*, **80**, 183 (1958).

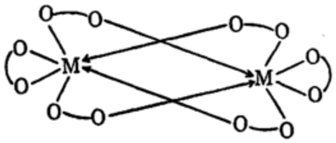
8) T. Moeller, E. Gulyas and R. H. Marshall, *J. Inorg. Nucl. Chem.*, **9**, 82 (1959).

9) G. W. Pope, J. F. Steinabach and W. F. Wagner, *ibid.*, **20**, 304 (1961).

10) S. N. Misra, T. N. Misra and R. C. Mehrotra, *Indian J. Chem.*, **3**, 525 (1965).



Where two metal octahedra are bridged through oxygen atoms of ligand molecule. The probability of following structure, however, could not be ruled out:



Where the oxygen atoms of ligands are donating electrons to empty d_π orbital of the metal.

Experimental

Glass apparatus with interchangeable joints was used. Anhydrous lanthanum, praseodymium, neodymium and samarium chlorides were prepared as described in earlier publications.11) Pure lanthanum, praseodymium and neodymium isopropoxides were prepared by sodium alkoxide method already reported12); solvents dried as described in earlier communication.11)

Molecular Weights. The molecular weights of these derivatives were determined ebullioscopically by semi-micro gallenkemp ebulliometer using thermistor sensing in refluxing benzene. The experimental

TABLE 1. REACTIONS OF ISOPROPOXIDES OF NEODYMIUM AND PRASEODYMIUM WITH BENZOYLACETONE AND DIBENZOYLMETHANE IN DIFFERENT RATIO

Reaction mixture in g.		Molar ratio	Formula, yield (g) and nature of the product	Analysis % Found Metal	Analysis % Found Isopropoxy	Analysis % Calculated Metal	Analysis % Calculated Isopropoxy
Praseodymium isopropoxide Benzoylacetone Benzene	1.132 0.561 86.0	1 : 1	$Pr\ (O\text{-}iC_3H_7)_2(O_2C_{10}H_9)$ Green crystalline solid 1.48	33.29	28.08	33.53	28.11
Neodymium isopropoxide Benzoylacetone Benzene	1.137 0.563 83.00	1 : 1	$Nd(O\text{-}iC_3H_7)_2(O_2C_{10}H_9)$ Pink microcrystalline solid 1.50	34.00	27.68	34.05	27.089
Praseodymium isopropoxide Benzoylacetone Benzene	1.087 1.091 78.00	1 : 2	$Pr(O\text{-}iC_3H_7)(O_2C_{10}H_9)_2$ Green crystalline solid 1.78	26.88	11.29	26.97	11.31
Neodymium isopropoxide Benzoylacetone Benzene	1.113 1.119 79.00	1 : 2	$Nd(O\text{-}iC_3H_7)(O_2C_{10}H_9)_2$ Pink microcrystalline solid 1.84	27.38	11.20	27.44	11.24
Praseodymium isopropoxide Benzoylacetone Benzene	1.321 1.893 76.00	1 : 3	$Pr(O_2C_{10}H_9)_3$ Green crystalline solid 2.50	22.42	—	22.54	—
Neodymium isopropoxide Benzoylacetone Benzene	1.001 1.50 75.00	1 : 3	$Nd(O_2C_{10}H_9)_3$ Pink microcrystalline solid 2.00	22.88	—	22.98	—
Praseodymium isopropoxide Dibenzoylmethane Benzene	1.002 0.704 76.00	1 : 1	$Pr(O\text{-}iC_3H_7)_2(O_2C_{15}H_{11})$ green crystalline solid 1.50	29.10	24.38	29.33	24.49
Neodymium isopropoxide Dibenzoylmethane Benzene	1.163 0.811 78.00	1 : 1	$Nd(O\text{-}iC_3H_7)_2(O_2C_{15}H_{11})$ Pink crystalline solid 1.65	29.60	23.96	29.70	24.03
Praseodymium isopropoxide Dibenzoylmethane Benzene	1.012 1.401 78.00	1 : 2	$Pr(O\text{-}iC_3H_7)(O_2C_{15}H_{11})_2$ Green crystalline solid 2.61	21.63	9.10	21.79	9.12
Neodymium isopropoxide Dibenzoylmethane Benzene	1.003 1.387 81.00	1 : 2	$Nd(O\text{-}iC_3H_7)(O_2C_{15}H_{11})_2$ Pink crystalline solid 2.00	22.06	9.00	22.16	9.07
Praseodymium isopropoxide Dibenzoylmethane Benzene	1.112 2.368 80.00	1 : 3	$Pr(O_2C_{15}H_{11})_3$ green crystalline solid 2.80	17.29	—	17.36	—
Neodymium isopropoxide Dibenzoylmethane Benzene	0.879 1.85 83.0	1 : 3	$Nd(O_2C_{15}H_{11})_3$ pink crystalline solid	17.52	—	17.72	—

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11) S. N. Misra, T. N. Misra and R. C. Mehrotra, *J. Inorg. Nucl. Chem.*, **27**, 105 (1965); *J. Indian Chem. Soc.*, **42**, 351 (1965).

12) S. N. Misra, T. N. Misra, R. N. Kapoor and R. C. Mehrotra, *Chem. & Ind.*, **1963**, 120.

TABLE 2. ALCOHOL-INTERCHANGE WITH *t*-BUTANOL

Compound taken in g	*t*-Butanol in g	Formula, nature and yield (g) of the product	Analysis of the metal		Isopropanol in azeotrope	
			Found %	Calcd %	Found (g)	Calcd (g)
$Pr(O\text{-}iC_3H_7)_2(O_2C_{10}H_9)$ 1.05	5.7	$Pr(O\text{-}tC_4H_9)_2(O_2C_{10}H_9)$ green crystalline solid, sparingly soluble in benzene but dissloves in refluxing ethanol. (1.09)	31.50	31.65	0.28	0.30
$Nd(O\text{-}iC_3H_7)_2(O_2C_{10}H_9)$ 1.00	6.3	$Nd(O\text{-}tC_4H_9)_2(O_2C_{10}H_9)_2$ Pink microcrystalline solid, sparingly soluble in benzene but dissolves in refluxing ethanol (1.03).	31.87	31.39	0.29	0.30
$Pr(O\text{-}iC_3H_7)(O_2C_{10}H_9)_2$ 1.30	5.9	$Pr(O\text{-}tC_4H_9)(O_2C_{10}H_9)_2$ Green solid, sparingly soluble in benzene but dissolves in refluxing ethanol (1.31).	26.28	26.28	0.15	0.15
$Nd(O\text{-}iC_3H_7)(O_2C_{10}H_9)_2$ 1.06	6.7	$Nd(O\text{-}tC_4H_9)(O_2C_{10}H_9)_2$ Pink solid, sparingly soluble in benzene but dissolves in refluxing ethanol (1.07).	26.58	26.72	0.13	0.14
$Pr(O\text{-}iC_3H_7)_2(O_2C_{15}H_{11})$ 0.98	6.8	$Pr(O\text{-}tC_4H_9)_2(O_2C_{15}H_{11})$ Green solid, sparingly soluble in benzene but dissolves in ethanol (0.98).	27.50	27.61	0.23	0.24
$Nd(O\text{-}iC_3H_7)_2(O_2C_{15}H_{11})$ 1.12	7.5	$Nd(O\text{-}tC_4H_9)_2(O_2C_{15}H_{11})$ Pink solid, sparingly soluble in benzene but dissolves in ethanol (1.14).	27.98	28.08	0.27	0.28
$Pr(O\text{-}iC_3H_7)(O_2C_{15}H_{11})_2$ 1.63	5.0	$Pr(O\text{-}tC_4H_9)(O_2C_{15}H_{11})_2$ Green solid, sparingly soluble in benzene but dissolves in refluxing ethanol (1.65).	21.20	21.33	0.14	0.15
$Nd(O\text{-}iC_3H_7)(O_2C_{15}H_{11})_2$ 1.78	4.7	$Nd(O\text{-}tC_4H_9)(O_2C_{15}CH_{11})_2$ Pink solid, sparingly soluble in benzene but dissolves in refluxing ethanol (1.81).	21.58	21.73	0.15	0.16

technique was the same as described in our earlier communication.[13]

Analytical Methods. Praseodymium was estimated as oxinate while lanthanum, neodymium and samarium were estimated by precipitating them as oxalate followed by the ignition to corresponding oxide. The isopropanol content of benzene-isopropanol azeotrope was determined by an oxidimetric method.[14]

Reaction between Praseodymium Isopropoxide and Benzoylacetone (Molar Ratio 1 : 3) in Benzene. The mixture of praseodymium isopropoxide (1.32 g) benzoylacetone (2.01 g) and benzene (84 g) was shaken thoroughly when a clear green solution was obtained. The reaction mixture was refluxed and the liberated isopropanol was fractionated out azeotropically with benzene. The product was obtained after distilling off excess solvent under reduced pressure.

Reaction of Praseodymium Di-isopropoxide Mono-benzoylacetonate with *t*-Butanol in Benzene. Praseodymium di-isopropoxide monobenzoylacetonate (1.43 g) benzene (83 g) and tertiary butanol (2.43 g) were refluxed under the column. After the removal of binary azeotrope (benzene - isopropanol), excess solvent was distilled out under reduced pressure and at the room temperature leaving a green micro-crystalline solid (Yield 1.56 g).

For brevity the reaction of isopropoxides of praseodymium and neodymium with benzoylacetone and dibenzoylmethane are summarised in Table 1, and those from the reaction between above derivatives and tertiary-butanol and summarised in Table 2.

Anhydrous Acetylacetonates of Lanthanum, Praseodymium Neodymium and Samarium. *a) Preparation of Ammonium Acetylacetonate*. Acetylacetone (18.3 g) was dissolved in benzene (150 g) and a current of anhydrous ammonia was slowly passed through the solution. The reaction was exothermic and a white crystalline solid separated out from the solvent. The completion of the reaction was indicated by cooling of

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[13] S. N. Misra, T. N. Misra and R. C. Mehrotra, *J. Inorg. Nucl. Chem.*, **25**, 195 (1963); **25**, 201 (1963).

[14] D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, **1950**, 3450.

Table 3.

Reaction mixture in g		Nature of the product	Analysis	
			% Metal Found	% Metal Calcd
Lanthanum chloride	2.47	$La(O_2C_5H_7)_3$, light yellow crystalline solid, soluble in refluxing ethanol but sparingly soluble in benzene.	31.90	31.84
in ethanol	57.00			
Amm. acetylacetonate	3.41			
Acetylacetone	10.0			
in ethanol	150.0			
Praseodymium chloride	2.03	$Pr(O_2C_5H_7)_3$ Green crystalline solid, soluble in refluxing ethanol but sparingly soluble in benzene.	32.0	32.15
in ethanol	54.0			
Amm. acetylacetonate	2.80			
Acetylacetone in	10.0			
ethanol	100.0			
Neodymium chloride	2.18	$Nd(O_2C_5H_7)_3$ Pink crystalline solid, soluble in refluxing ethanol but sparingly soluble in benzene.	32.48	32.67
in ethanol	60.0			
Amm. acetylacetonate	3.14			
Acetylacetonate in	10.0			
ethanol	153.0			
Samarium chloride	2.00	$Sm(O_2C_5H_7)_3$ Yellow crystalline solid, soluble in refluxing ethanol but insoluble in benzene.	33.36	33.59
in ethanol	60.0			
Amm. acetylacetonate	2.70			
acetylacetone	10.0			
in ethanol	190.0			

the reaction mixture. It was filtered, washed thoroughly with benzene and dried under reduced pressure (Yield 19.0 g).

b) Preparation of Lanthanum Triacetylacetonate. Lanthanum chloride (2.47 g) was dissolved in ethanol (87 g) when a clear solution was obtained. Ammonium acetylacetonate (3.41 g) taken in ethanol (89 g) containing 10.0 g of acetylacetone, was added to alcoholic lanthanum chloride solution when a white solid separated out. Excess acetylacetone most probably checks the alcoholysis of the product. On evaporating off the excess solvent a faint yellow crystalline solid sparingly soluble in benzene but soluble in refluxing ethanol and benzene was obtained (Yield 4.09 g).

The preparation of the anhydrous acetylacetonates of lanthanum, praseodymium, neodymium and samarium is summarised in Table 3.

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