Neodymium Benzoyltrifluoroacetonate Adducts Formed with Alcohols, Pyridine and Amines

Tsunenobu SHIGEMATSU and Takaharu HONJYO*

(Shigematsu Laboratory)

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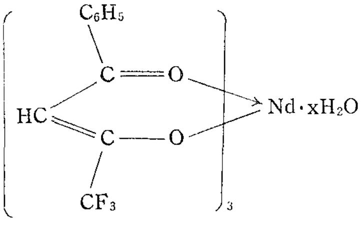
The composition and the properties of solid adducts of neodymium benzoyltrifluoroacetonate formed with alcohols, pyridine and amines were investigated by the techniques of elementary analysis, thermogravimetry, differential thermal analysis, infra-red, visible and ultraviolet spectrophotometry.

The composition of the solid adducts with alcohols and pyridine was expected as $Nd(C_{10}H_6O_2F_3)_3 \cdot H_2O \cdot 2ROH$ and $Nd(C_{10}H_6O_2F_3)_3 \cdot H_2O \cdot 2C_5H_5N$. The properties of their adducts were very similar. Amines formed two type adducts; $Nd(C_{10}H_6O_2F_3)_3 \cdot H_2O \cdot RNH_2$ and $Nd(C_{10}H_6O_2F_3)_2 \cdot OH \cdot RNH_2$, the latter of which was prepared in the presence of excess amines. Both the adducts were more stable than the alcohol or pyridine adducts.

INTRODUCTION

The solvent extraction of europium ions with benzoyltrifluoroacetone is enhanced by the addition of an active oxygen or nitrogen-containing Lewis base to the extraction system[1]. Such a phenomenon has generally been called the synergistic effect and may be attributed to the adduct formation between metal chelates and organic bases. Therefore, it has been recognized that the preparation of the solid adduct compounds and the appreciation of their chemical and physical properties are a very interesting problem. In recent years, the rare earth β-diketonates, especially europium chelates have been attended to the possible application in laser materials and studied by many investigators, and a number of new type europium β-diketonates or adducts with oxygen- or nitrogen-containing Lewis bases have been discovered[2~7].

In this research, the composition and the properties of solid adducts of the neodymium benzoyltrifluoroacetonate, [I], formed with alcohols, pyridine and amines were studied.



[I] (x = 2 or 3)

	Calcd.		Found
	x=2	x=3	
Nd_2O_3 (%)	20.4	19.9	19.6
C (%)	43.64	42.71	43.62
H (%)	2.69	2.87	2.87
M.P.	(97~101°C)		

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* 重松恒信，本浄高治

EXPERIMENTAL

Materials.——Neodymium oxide, 99.0 per cent purity, was obtained from Shin Nippon Kinzoku Co., Ltd. Benzoyltrifluoroacetone was obtained from the Dojindo Co., Ltd., Research Laboratories. Organic reagents such as benzene, *n*-hexane, acetone, alcohols etc. were purified by distillation. All the other reagents were the reagent-grade materials. Preparation of neodymium benzoyltrifluoroacetonate. ——Neodymium chelate (hydrate) was prepared by the following procedure. To 25 m*l*. of an aqueous solution of neodymium chloride (containing 1 g of the chloride), which is controlled to pH=6~7 by adding a dilute sodium hydroxide solution, an equivalent amount of benzoyltrifluoroacetone dissolved in 25 m*l* of acetone is added slowly with stirring. The pH of the resulting soluting is always maintained at a value just below that, at which neodymium hydroxide begins to precipitate, by the addition of either dilute sodium hydroxide or hydrochloric acid.

The mixed solution is stirred for more than twenty hours at 30°C to allow to complete the reaction. When acetone is evaporated and the chelate precipitates, the supernatant is decanted and discarded. The product is dissolved in *n*-hexane containing acetone just enough to dissolve the product, and washed with water. The organic layer is separated and the solvent is removed by the evaporation at room temperature. Redish purple needle crystals thus obtained are recrystallized from benzene and then dried over silica gel in a desiccator.

Preparation of neodymium benzoyltrifluoroacetonate adducts.——The alcohol adducts were prepared as follows. One gram of neodymium benzoyltriluoroacetonate hydrate is dissolved in 20 m*l*. of benzene or *n*-hexane by shortly warning. After 2 m*l*. of ethyl- or butyl-alcohol is added, the solution is allowed to stand at room temperature to remove the excess solvents. The product which is formed as a viscous liquid at first, is crystallized by repeating the dissolving with a small amont of benzene or *n*-hexane and evaporating the excess solvent. Redish purple needle crystals thus obtained are dried over silica gel in a desiccator. The amine (ethylamine or *n*-butylamine) and pyridine adducts were prepared in the same procedure. The pyridine adduct was similar in appearence to the alcohol adducts, while the amine adducts were obtained as a white powder.

Another amine adduct was obtained, when neodymium benzoyltrifluoroacetonate reacted with an equivalent amount of amine in benzene, followed by the removal of benzene under the low pressure. By this process any pyridine adduct was not produced.

Carbon, hydrogen, nitrogen and neodymium were analysed: Neodymium was determined gravimetrically by igniting the compounds into the oxide, according the method described by Pope *et al*[8]. Melting points were measured with a Yanagimoto Micro Melting Point Apparatus. Differential thermal analysis and thermogravimetric analysis.——The DTA and the TGA curves were obtained with a Shimadzu Automatic Differential Thermal Apparatus, Type DT-10 and a Shimadzu Automatic Thermo Gravimetric Analysis Apparatus, Type TB-10. For some of the samples, a Rigaku Denki Automatic Differential Thermobalance Analysis Apparatus was also used. Samples (40~100 mg) packed in a platinum or quartz container were heated in air or a stream (50 m*l*./min) of nitrogen. The heating rate of the furnance was kept at constant in the range of from 2.5°C/min to 10°C/min. Weight and heat changes were recorded automatically as a function of temperature, which was measured with a alumel-chromel thermocouple.

Infra-red spectra.—— Infra-red absorption spectra were obtained by the KBr disk method with a Perkin Elmer Grating Infra-red Spectrophotomer, Model 521.

Visible and ultra-violet spectra.——Visible and ultra-violet absorption spectra were obtained with a Shimadzu Automatic Recording Spectrophotometer, Model UV 50, using 1 cm. qualtz cells.

RESULTS AND DISCUSSION

Composition and Solubility.—— From the data of the elementary analysis, it is expected that the hydrate includes two or three moles of water. At room temperature, the hydrate is moderately soluble in *n*-hexane or benzene, but readly dissolved into alcohols or acetone to show a bluish purple color. The results of the elementary analysis and the melting points of the various adducts are summarized in Table 1. The alcohol adducts and the pyridine adduct contain two moles of alcohols and of pyridine, respectively, and these adducts are very soluble in alcohols or acetone, showing a bluish purple color. Into benzene, the alcohol adducts are not so easily dissolved, whereas the pyridine adduct is readily dissolved. The data of the elementary analysis indicate the existence of two kinds of the amine adducts having a different composition each other: Although both of the adducts contain one mole of the amine, the mole-ratio of the chelating agent to the metal is considered to be two for the adducts produced in the presence of the excess amine, but to be three for the adducts prepared by adding the equivalent amount of the amine. Therefore, those adducts will be distinguished to be the MR_2L-type adducts and the MR_3L-type adducts, respectively. All the amine adducts are very soluble in amine, but not so much in benzene, alcohol or acetone.

Table 1. Neodymium benzoyltrifluoroacetonate adducts.

Adduct	Formula*	Nd_2O_3 (%) Calcd.	Nd_2O_3 (%) Found	N (%) Calcd.	N (%) Found	m.p. (°C)
Ethyl alcohol	$(C_{10}H_6O_2F_3)_3\cdot Nd\cdot H_2O\cdot 2C_2H_5OH$	18.7	18.7	—	—	84~ 88
n-Butyl alcohol	$(C_{10}H_6O_2F_3)_3\cdot Nd\cdot H_2O\cdot 2C_4H_9OH$	17.6	17.2	—	—	84~ 88
Pyridine	$(C_{10}H_6O_2F_3)_3\cdot Nd\cdot H_2O\cdot 2C_5H_5N$	17.4	18.0	2.91	2.70	87~ 92
Ethyl amine	$(C_{10}H_6O_2F_3)_2\cdot Nd\cdot OH\cdot C_2H_5NH_2$	26.5	27.6	2.20	1.60	225~230
n-Butyl amine	$(C_{10}H_6O_2F_3)_2\cdot Nd\cdot OH\cdot C_4H_9NH_2$	25.3	26.8	2.11	2.24	225~230
n-Butyl amine	$(C_{10}H_6O_2F_3)_3\cdot Nd\cdot H_2O\cdot C_4H_9NH_2$	19.1	20.4	1.59	1.85	205~207

*Existence of H_2O molecule or OH group is assumed.

Heat stability.——The TGA and DTA curves of the adducts are shown in Fig. 1. The weight loss happens gradually near the melting points and at that time, one or two molecules of the adduct-forming organic bases are desolvated in the case

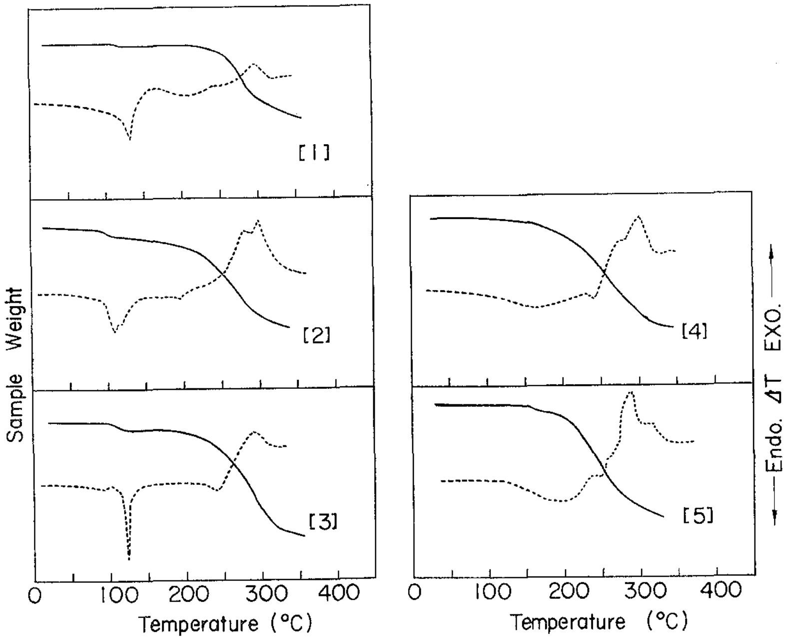

Fig. 1. Differential themal analysis and thermogravimetric analysis curves of neodymium benzoyltrifluoroacetonate and its adducts:
[1] Hydrate [2] Ethyl alcohol and *n*-Butyl alcohol adduct
[3] Pyridine adduct [4] Ethyl amine and *n*-Butyl amine adduct
(MR$_2$L type adduct) [5] *n*-Butyl amine adduct (MR$_3$L type adduct)

of the alcohol adducts, pyridine adduct and the MR$_3$L-type amine adduct. The compounds start to decompose above about 200°C.

The endothermal peak of the DTA curves corresponds to the desolvation of the donor molecules and the melting of the adduct compounds, while the exothermal peak is due to the decomposition of the compounds.

Two molecules of alcohols are almost simultaneously desolvated at 60~130°C, in the alcohol adducts. Pyridine molecules are stepwisely removed: The first desolvation of the pyridine molecules occurs at 60~130°C and the second desolvation at a higher temperature. However, when heated with the rate less than 1°C/min., the desolvation of the two pyridine molecules takes place at the same time.

A distinct difference is observed between the TGA curves of the MR$_3$L-type amine adduct and of the MR$_2$L-type amine adducts: The MR$_3$L-type adduct represents the similar shaped TGA curve to the alcohol or the pyridine adducts, whereas the MR$_2$L-type adducts do not show a characteristic weight loss, which appears near the melting point of the alcohol, pyridine or the MR$_3$L type amine adduct. However, these two type amine adducts show the similar shaped DTA curves; that is the endothermal peak is not so sharp as seen in the DTA curves of the alcohol or the pyridine adducts.

The heat stability of the neodymium benzoyltrifluoroacetonate adducts formed with alcohols, pyridine and amines increases in the next order; pyridine adduct$\approx$ alcohol adducts$<$amine adducts.

Infra-red spectra.——The infra-red absorption spectra of the neodymium benzoyltrifluoroacetonate adducts are shown in Fig. 2. The infra-red spectra of the adducts are very similar to that of the hydrate chelate. It is impossible to estimate each spectrum of the adducts because of their complexity, but the assignment of the donor molecules in the adducts can be identified by the individual spectra.

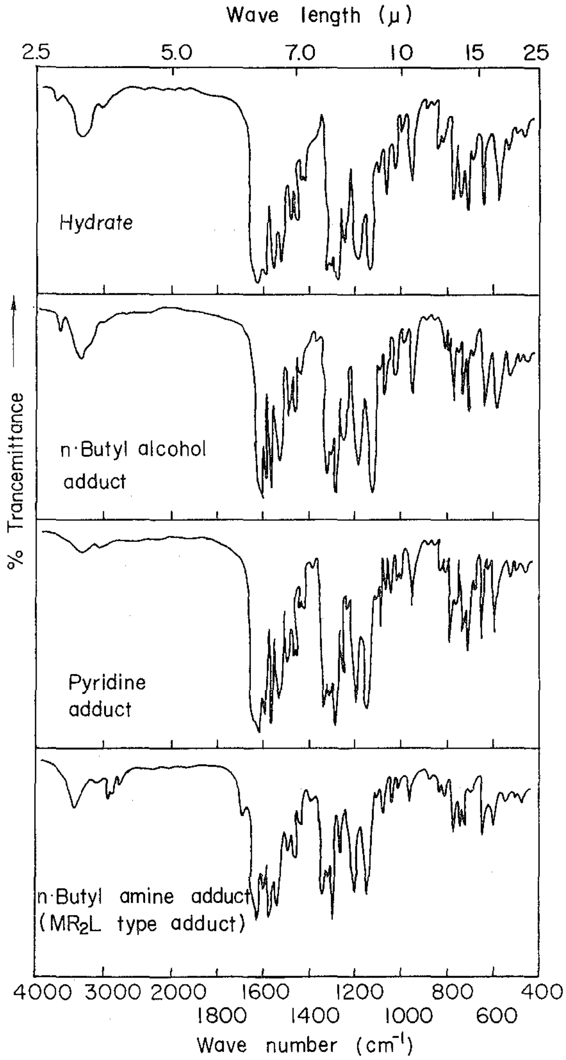

Fig. 2. Infra-red absorption spectra of neodymium benzoyltrifluoroacetonate and its adducts.

n-Butyl alcohol adduct······3645 cm^{-1} is due to OH stretching vibration.

Pyridine adduct······1217 (1215), 1035 (1031), 1003 (990), 752 (748) and 608 (604) cm^{-1} belong to adduct pyridine molecules.

n-Butyl amine adduct······2955 (2955), 2930 (2925) and 2865 (2860) cm^{-1} are caused by adduct amine molecules. The values of the wave number in the blackets show the single spectrum of the adduct molecules.

The spectra of the two type amine adducts have quite the same shape, but the MR_2L-type adduct shows the weaker absorption than the MR_3L-type adduct (and also than the hydrate and the other adducts) over the whole wave length, and a new band appears at 1675 cm^{-1} in the spectrum of the former adduct, but not of the latter adduct.

Visible and ultra-violet spectra.——Figure 3 and 4 indicates the visible and ultraviolet absorption spectra of the solutions prepared by dissolving neodymium benzoyltrifluoroacetonate in *n*-hexane containing ethyl alcohol, pyridine or *n*-butylamine: The mole-ratio of the adduct-forming compounds to the chelate is 3:1 in all cases, because when the ratio is less than 2, the solutions are too unstable to measure the absorption. The wavelengths of the absorption spectra are summarized in Table 2.

Table 2. Visible and ultraviolet absorption spectra of neodymium benzoyltrifluoroacetonate in *n*-hexane containing alcohol, pyridine and amine.

Compound	Organic base	λmax (mμ)
Hydrate	Ethyl alcohol or Pyridine	512, 526, 571, 582, 322
	n-Butyl amine	515, 525, 583, 310

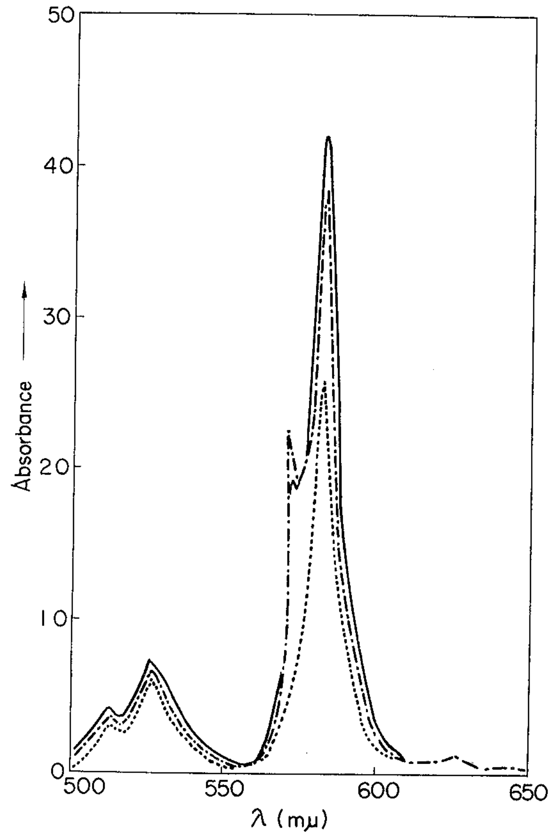

Fig. 3. Visible absorption spectra of neodymium benzoyltrifluoroacetonate (2×10^{-2}M) in *n*-hexane containing 6×10^{-2}M of ethyl alcohol, —·—; pyridine, ——; or *n*-butyl amine, -------.

The visible spectra shown in Fig. 3 are quite the same as that of the ethyl alcohol, pyridine or *n*-butyl amine solutions of the hydrate chelate, and as seen in the figure, (i) the absorption intensity decreases in the followihg order; pyridine $>$ethyl alcohol$>$*n*-butyl amine; (ii) The absorption maximum of the solution containing amine shifts slightly to a longer wave length than that of other solutions: And (iii) at 571 mμ, the solution containing alcohol shows a small, but sharp absorption band, the solution containing pyridine shows a distinct shoulder, while the solution containing amine give neither such a band nor a shoulder. The change of the band at 571 mμ is based on the electronic transitions between two energy levels involving the 4f orbitals by chelate formation or adduct formation. The electronic fields imposed upon the central metal ions by the surrounding anions or Lewis bases9).

As shown in Fig. 4, the ultra-violet absorption spectra of the solution containing alcohol is the same as that of the solution containing pyridine, but the absorption band of the solution containig amine shifts to a shorter wave length. The absorption band of ultra-violet regions is due to the benzoyltrifluoroacetonate structure and arised from the electronic transitions of the bound benzoyltrifluoroacetonate ions such as $\pi \rightarrow \pi^*$ transition10).

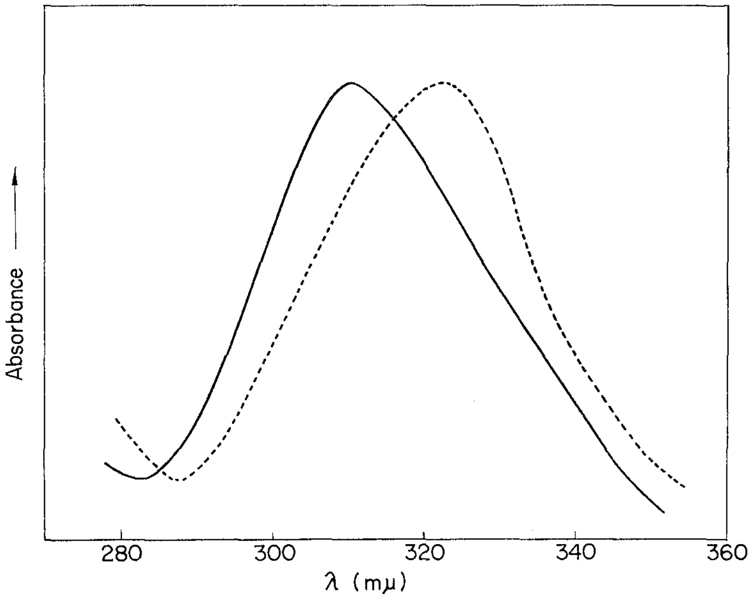

Fig. 4. Ultra-violet absorption spectra of neodymium benzolytrifluoroacetonate (2×10^{-5}M) in *n*-hexane containing 6×10^{-5}M of ethyl alcohol, ——; pyridine, ——; or n-butyl amine, -------.

The results of the visible and ultra-violet spectra may indicate that the interaction between the neodymium benzoyltrifluoroacetonate and alcohols in *n*-hexane is almost the same with that in the case of pyridine, but quite different from that in the case of amines.

From the results of the elementary analysis, the heat stability and the visible and ultra-violet spectra, it is expected that the alcohol adducts and the pyridine adduct have similar composition and properties. From the vaporpressure studies of the rare-earth acetylacetonate adducts with alcohol, it was suggested that two molecules of alcohol bond to ligand molecules of the acetylacetonate monohydrate by dipole-dipole interaction or strong hydrogen bonding[8,11]. Although it is impossible to confirm the bonding state of the adduct molecules in the present time, the composition of the solid adducts with alcohols or pyridine are considered as $Nd(C_{10}H_6O_2F_3)_3 \cdot H_2O \cdot 2ROH$ or $Nd(C_{10}H_6O_2F_3)_3 \cdot H_2O \cdot 2C_5H_5N$. And from this composition of the adduct, it is deduced that the neodymium benzoyltrifluoroacetonate crystallized is the tri-hydrate rather than di-hydrate. In other word, two moles of alcohol or pyridine react with the neodymium chelate, trihydrate to form the adduct by replacing two moles of water.

The results of the elementary analysis, the heat stability and the infra-red spectra show that amines form two type adducts as described above of which, the MR_3L-type adducts behave in the similar manner with the alcohol or pyridine adducts, whereas the MR_2L-type adducts, differently. The composition of the former is assumed therefore as $Nd(C_{10}H_6O_2F_3)_3 \cdot H_2O \cdot RNH_2$ and that of the latter may be $Nd(C_{10}H_6O_2F_3)_2 \cdot OH \cdot RNH_2$. The amine adducts are generally more stable than the alcohol or pyridine adducts, and the latter type adduct is particularly stable. From such experimental results, it is expected that the latter type adduct is dimer species, which is produced in the presence of excess amines.

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