Adducts of Neodymium(III) and Lanthanum(III) Acetylacetonate with some Bidentate Organic Bases[1]

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Several bidentate uncharged organic base adducts of neodymium(III) and lanthanum(III) acetylacetonate were prepared by the reaction of the free bases with tris(acetylacetonato)neodymium(III) monohydrate and tris-(acetylacetonato)lanthanum(III) dihydrate in ethyl acetate, respectively. Elemental analyses, molecular weight determinations, NMR, IR, and visible absorption spectra indicate that the adducts are of the general formula $Ln(AA)_3(BB)$, where AA, BB, and Ln denote acetylacetonate ion, bidentate uncharged base and lanthanide ion, respectively. Thermal stability of the base adducts as well as the hydrates was studied by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Coordination of the additional ligand having reactive hydrogen atoms resulted in poor thermal stability of the addition complexes. This might be explained by assuming that the coordinated acetylacetonate ion reacts readily with the reactive hydrogen atom of the neighboring ligand to liberate acetylacetone molecule, though the nature of the resulting pyrolyzed products is unknown.

It is well-known that the reaction of a lanthanide ion with acetylacetone in an aqueous solution affords always hydrated chelates[2,3] of hepta-[4,5] or octa-coordinate[6,7] structure. Dehydration from the hydrated chelates gave no anhydrous lanthanide acetylacetonate but a polymerized hydroxo chelate by liberating an acetylacetone molecule.[3,8] Przystal and his co-workers[9] obtained anhydrous chelates by the reaction of lanthanide hydrides with acetylacetone. However, the anhydrous chelates hydrolyzed easily to the hydroxo complex accompanied by weight loss when they were exposed to the moist air.

With the hope of obtaining thermally stable lanthanide complexes,[10] bidentate organic base adducts of tris(acetylacetonato)neodymium(III) and -lanthanum-(III) were prepared.

The organic bases used were ethylenediamine(en), 1,2-propanediamine(pn), 2,2′-dipyridyl(2-dipy), 4,4′-dipyridyl(4-dipy), 1,10-phenanthroline(phen), and isopropanolamine(ipa). These uncharged bidentate bases are expected to occupy the coordination sites of hydrated water to afford the mixed ligand uncharged complexes of the general formula of $Ln(AA)_3(BB)$, where AA, BB and Ln denote acetylacetonate ion, bidentate base and lanthanide ion, respectively. The structures and thermal properties of these addition complexes were studied.

Experimental

Materials. Lanthanide nitrates, organic bases and acetylacetone were of reagent grade and used without further purification. Chloroform and pyridine used for spectral measurements were dried and distilled according to standard procedures.

Preparation of Addition Complexes. Neodymium and lanthanum acetylacetonate of unknown degree of hydration, prepared by a slight modification of the standard procedure,[2] were recrystallized from ethyl acetate and the products were dried at room temperature to obtain $Nd(AA)_3 \cdot H_2O$ and $La(AA)_3 \cdot 2H_2O$[11] respectively, their compositions being confirmed by elemental analyses.

The base adduct was prepared by dissolving 0.8 g of a hydrated complex in 25 ml of warm (60—70 °C) ethyl acetate containing an appropriate amount of an organic base. The insoluble residue was filtered off after about ten minutes and the filtrate was cooled to about 0 °C. The neodymium-(III) and lanthanum(III) adducts precipitated as red-purple and white crystalline products, respectively. They were collected by filtration, and dried at room temperature under reduced pressure. Yield: 40—80%. Results of elemental analyses are shown in Table 1.

Diaquo complex, $Nd(AA)_3 \cdot 2H_2O$[11] was also prepared by recrystallizing 0.8 g of monohydrate from about 25 ml of ethyl acetate–water–acetone mixture (90: 5: 5 in volume). Similarly mono pyridine adduct of the formula $Ln(AA)_3(Py)-(H_2O)_2$ was obtained by recrystallizing 0.8 g of the corresponding dihydrate from 20 ml of warm pyridine–cyclohexane mixture (95: 5). Compositions of these complexes were confirmed by elemental analyses.

Measurements. IR measurements were carried out with a JASCO-DS-403G spectrophotometer. A Hitachi-124 spectrophotometer was used to observe visible absorption spectra. DTA was measured with Rigaku Denki-thermoflex-8001 in nitrogen atmosphere using α-alumina as a reference. TGA was measured with a Shimadzu-thermobalance TB-10B in a nitrogen stream. The thermal analyses were carried out mostly at a heating rate of 10 °C min^{-1}. NMR spectra were obtained by use of a Varian A-60 NMR spectrometer in deuterated chloroform using TMS as an internal reference. Molecular weight was determined with a Mechrolab 301A vapor pressure osmometer.

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Table 1. Analytical results

Compound	Molecular formula	Elemental analysis C% Found	C% Calcd	H% Found	H% Calcd	N% Found	N% Calcd
$Nd(AA)_3(en)$	$C_{17}H_{29}N_2O_6Nd$	40.68	40.72	5.51	5.78	5.78	5.59
$Nd(AA)_3(pn)$	$C_{18}H_{31}N_2O_6Nd$	41.71	41.94	6.07	6.01	5.40	5.49
$Nd(AA)_3(2\text{-dipy})$	$C_{25}H_{29}N_2O_6Nd$	50.00	50.25	5.05	4.85	4.66	4.69
$Nd(AA)_3(4\text{-dipy})$	$C_{25}H_{29}N_2O_6Nd$	49.45	50.25	5.10	4.85	4.57	4.69
$Nd(AA)_3(phen)$	$C_{27}H_{29}N_2O_6Nd$	52.27	52.17	5.07	4.67	4.27	4.51
$Nd(AA)_3(ipa)$	$C_{18}H_{30}NO_7Nd$	41.17	41.86	5.91	5.81	3.02	2.71
$La(AA)_3(en)$	$C_{17}H_{29}N_2O_6La$	41.26	41.16	5.80	5.85	4.27	4.51
$La(AA)_3(pn)$	$C_{18}H_{31}N_2O_6La$	41.93	42.38	5.91	6.08	5.43	5.49
$La(AA)_3(ipa)$	$C_{18}H_{30}NO_7La$	41.38	42.30	5.89	5.87	2.90	2.74
$La(AA)_3(phen)$[a]	$C_{27}H_{29}N_2O_6La$	52.47	52.62	4.74	4.71	4.53	4.55

a) The product as isolated from an ethyl acetate solution contained one mole of ethyl acetate as a lattice solvent. Found: C, 52.42; H, 4.86; N, 4.16%. Calcd for $La(AA)_3(phen)$ (ethylacetate): C, 52.94; H,5.12; N, 3.98%. IR(Nujol): $\nu_{C=O}$= 1732 cm^{-1}. NMR in $CDCl_3$ (TMS reference): 1.27_t ($-CH_2C\underline{H}_3$); 2.05_s ($C\underline{H}_3CO$); 4.16 ppm_q ($-C\underline{H}_2CH_3$). Ethylacetate can be removed by drying at about 80°C under reduced pressure to give a complex having the formula shown in the table.

Results and Discussion

Structures of Complexes. The structures of the addition complexes were elucidated by IR, visible and NMR spectral data.

Elemental Analysis and Molecular Weight. Results of elemental analyses (Table 1), indicate the formation of a 1: 1 addition complex with each bidentate base, suggesting that the bidentate base occupies the coordination sites of hydrated water through ligand exchange reaction.

Table 2. Molecular weights(37 °C)

Compound	Molecular weight Found	Molecular weight Calcd	Solvent
$Nd(AA)_3(pn)$	532	515.44	Pyridine
$La(AA)_3(pn)$	548	510.11	Pyridine
$Nd(AA)_3(phen)$	564	621.53	Pyridine
$La(AA)_3(phen)$	601	616.20	Chloroform
$Nd(AA)_3(2\text{-dipy})$	620	597.51	Pyridine
	810		Chloroform
$Nd(AA)_3(4\text{-dipy})$		597.51	
	327		Pyridine

Molecular weights of the bidentate base adducts were measured with a vapor pressure osmometer. Results are summarized in Table 2 together with solvents used. Observed values agreed fairly well with those calculated from the formula of mononuclear 1: 1 adducts, except for the 4,4′-dipyridyl adduct. Thus, the addition complexes, with exception of the 4,4′-dipyridyl adduct, can be considered to be of octa-coordinated mononuclear structure.

As regards the 4,4′-dipyridyl adduct, both terminal nitrogen atoms can not coordinate to the central metal ion simultaneously, and the resulting adduct may be of polymeric form bridged by 4,4′-dipyridyl. The 4,4′-dipyridyl adduct in chloroform showed a molecular weight slightly larger than that corresponding to the monomeric structure, suggesting that the depolymerization occurred upon dissolution of the polymeric complex in chloroform. On the other hand, the molecular weight of the adduct in pyridine was half the value of monomeric form, showing the complete dissociation of 4,4′-dipyridyl from the addition complex by coordination of pyridine molecule.

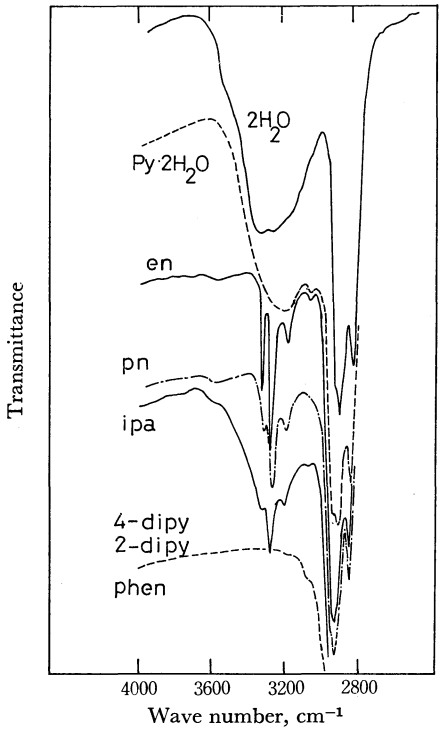

Fig. 1. IR spectra of $Ln(AA)_3(BB)$ in which BB represents the respective base (or bases) indicated in the figure.

Infrared Spectra. IR spectra of the base adducts as well as the hydrated complexes are given in Fig. 1 in the region 2800—4000 cm^{-1}. The dihydrate and the pyridine adducts show a relatively intense and broad absorption at about 3200—3300 cm^{-1} region due to ν_{OH}, and at about 1670—1690 cm^{-1} region due to δ_{OH} of water.[11]

Table 3. Absorption bands (500—600 nm) of neodymium complexes

Compound	Solvent	Absorption peak(nm) / Molar absorptivity									
$Nd(AA)_3(en)$	$CHCl_3$	513	525	528	572	575_{sh}	581	584_{sh}	587	598	
		2.9	5.2	5.2	19.0	12.5	22.8	19.6	17.1	4.5	
	Py	513		527	571	575_{sh}	581				
		2.8		5.8	22.6	14.6	28.7				
$Nd(AA)_3(pn)$	$CHCl_3$	513	525	528	572	575_{sh}	581	584_{sh}	587	598_{sh}	
		2.3	4.4	4.6	19.6	11.8	22.6	18.9	16.6	4.3	
	Py	512		527	571	575_{sh}	581				
		2.4		5.7	24.0	14.7	28.5				
$Nd(AA)_3(ipa)$	$CHCl_3$	513		527	571	575_{sh}	581	584	587	598_{sh}	
		2.4		5.1	17.7	13.8	22.6	21.1	18.2	4.9	
	Py	512		527	571	575_{sh}	581	583			
		2.7		6.4	23.0	15.1	28.4	27.4			
$Nd(AA)_3(2\text{-dipy})$	$CHCl_3$	513		526	571	575_{sh}	582	584	588	591	598_{sh}
		2.1		4.5	17.4	12.7	20.6	17.8	15.0	12.0	4.9
	Py	512		527	571	575_{sh}	581	583			
		2.1		7.0	23.1	16.4	31.4	32.5			
$Nd(AA)_3(phen)$	$CHCl_3$	514		527	572	576	582	585	588	593	600_{sh}
		2.2		5.1	21.2	13.8	22.2	17.7	15.6	11.4	4.2
$Nd(AA)_3(4\text{-dipy})$	$CHCl_3$	513		526	571	575_{sh}	582	584	589	591	598_{sh}
		2.4		4.9	15.5	12.8	20.8	19.0	15.7	12 3	3.0
	Py	512		527	571	575	581	583			
		3.1		7.4	23.1	16.7	31.8	33.1			

On the other hand, 2,2′-dipyridyl, 4,4′-dipyridyl and 1,10-phenanthroline adduct show no absorption band due to water molecule. Ethylenediamine and 1,2-propanediamine adducts show sharp triplet absorptions in the 3300 cm^{-1} region due to ν_{NH}. Isopropanolamine adducts show a rather complicated spectra in the 3300 cm^{-1} region due to the superimposition of ν_{NH} and ν_{OH}.

IR absorptions of the β-diketone moiety of these addition complexes appear at 1590—1600 and 1510—1520 cm^{-1} for $\nu_{C=O}$ and $\nu_{C=C}$, respectively.[11,12]

Visible Absorption Spectra of Neodymium Complexes. Visible absorption spectra of the 2,2′-dipyridyl adducts are shown in Fig. 2 and the numerical data for a series of neodymium complexes in Table 3 in the range 500—600 nm. The spectral characteristics of the base adducts are very similar to each other regardless of the kind of base. The absorption intensity was found to be higher in pyridine than in chloroform. A similar increase in absorption intensity was observed when excess bidentate base was added to the chloroform solution of the corresponding addition complex.

Although the shape of absorption band of the base adduct in chloroform is similar to that for neodymium β-diketonates[13] believed to be heptacoordinate, the present addition complexes are definitely octacoordinate even in chloroform solution as evidenced by NMR spectra. Thus, the diagnosis on the coordination structure of lanthanide chelates from the hypersensitive absorption bands may be useful only within a limited

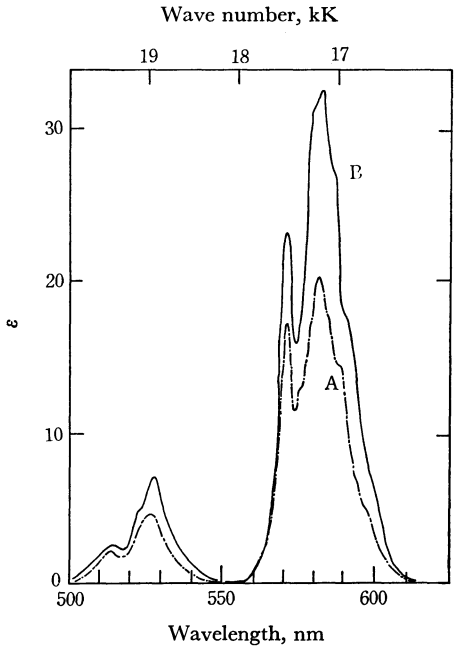

Fig. 2. Visible absorption spectra of $Nd(AA)_3$ (2-dipy) in chloroform(A) and pyridine(B).

combination of ligands.[13,14]

NMR Spectra of Lanthanum Complexes. NMR spectral data for several addition complexes of lanthanum(III) are summarized in Table 4. NMR signals of acetylacetone moiety of the complexes appear at 1.73—1.87 ppm for methyl protons and at 5.19—5.30 ppm for methine proton as a relatively broad singlet

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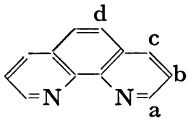
Table 4. Proton NMR absorption peaks of lanthanum complexes in deuteriochloroform(TMS reference)

Compound	Chemical shift (ppm)		
$La(AA)_3(en)$	$1.85_s(CH_3)$	$1.98_s(NH_2)^u$	$2.76_s(CH_2)^u$
	$5.30_s(CH)$		
en	$1.27_s(NH_2)^u$	$2.72_s(CH_2)^u$	
$La(AA)_3(pn)$[e]	$1.08_d(CH_3)^u$	$1.87_s(CH_3)$	$2.14_s(NH_2)^u$
	$5.22_s(CH)$		
$CH_3{}^dCH^e(NH_2)CH^bH^aNH_2$	$1.03_d(CH^d{}_3)^u$	$1.48_s(NH_2)^u$	$2.38_q(CH^a)^u$
	$2.68_q(CH^b)^u$	$2.76_{hd}(CH^e)^u$	
$La(AA)_3(phen)$	$1.73_s(CH_3)$	$5.19_s(CH)$	$7.63_q(H^b)^u$
	$7.78_s(H^d)^u$	$8.30_q(H^c)^u$	$9.41_q(H^a)^u$
	$7.56_q(H^b)^u$	$7.71_s(H^d)^u$	$8.19_q(H^c)^u$
	$9.14_q(H^a)^u$		

s) Singlet peak. d) Doublet peak. q) Quartet peak. hd) Sixteen multiplet peak. u) proton signals of the uncharged base. e) A part of proton signals could be assigned as shown in table, multiplet peaks of others appearing at 2.3—2.9 ppm region.

Superscripts, a, b, c, ·····, denote the signals from the corresponding protons indicated on the structural formula.

peak. Other signals can be assigned to those of the base coordinated to the complexes.

Amine protons of the free ethylenediamine and 1,2-propanediamine are known to give a singlet peak, while those of the coordinated ligands were found to shift remarkably to the lower field (0.71 ppm for ethylenediamine and 0.66 ppm for propanediamine). This deshielding effect of the amine protons obviously suggests the coordination of amino groups to the lanthanide ion.

Deshielding shifts of proton signals due to ethylene- or propylene moiety of the corresponding coordinated diamines were apparent but very slight. A remarkable change in the adduct formation arose on the spin-spin coupling constants, presumably due to fixation of the most favorable conformation for chelation of the metal ion. The coupling constants of the ring protons on a rigid 1,10-phenanthroline nucleus in $La(AA)_3(phen)$ remained equal to those in the free base, although the signals appeared at 0.27—0.07 ppm field lower than those of the free base.

Base adducts of paramagnetic neodymium chelate showed very broad proton signals, giving no high resolution signals due to base. This suggests that the coordinated base did not dissociate from the neodymium(III) adduct in deuteriochloroform.

The structure of base adducts of the general formula $Ln(AA)_3(BB)$ is very likely to be of a mononuclear octa-coordination, in which each of three acetylacetonate ion and an uncharged bidentate base occupy *cis*-coordination sites.[15] In the case of 4,4′-dipyridyl adducts, the structure is still octa-coordinate but may be polymeric. The coordination site of the base is not certain.

Thus it is interesting to note that most unidentate uncharged bases gave no bis-adduct with acetylacetonate chelate under similar conditions. For example, pyridine afforded a mono pyridine adduct of the general formula $Ln(AA)_3(Py)(H_2O)_2$ when the hydrated chelate was recrystallized from pyridine. The only known example for bis-base adduct is of dipivaloylmethane chelates such as $Eu(DPM)_3(Py)_2$[16] and $Ho(DPM)_3$-$(4\text{-pic})_2$,[17] where DPM and 4-pic denote dipivaloylmethanate ion and 4-picoline, respectively.

The relative lower preference of forming bis-adduct with unidentate base in comparison with bidentate base can be understood to be due to the chelate effect of the latter. The formation of bis base adduct of dipivaloylmethane chelates can then be ascribed to the increased hydrophobic interaction between the hydrocarbon moieties of the diketone ligand and water molecules.

Thermal Properties. Thermal properties of the addition complexes were examined by DTA and TGA methods. Those of the hydrate complexes were also studied for comparison. Numerical data are summarized in Table 5.

$Nd(AA)_3(H_2O)_2$ released one mole of water at 68 °C giving a monohydrate, which subsequently liberated one-half mole of acetylacetone at 110—116 °C. Residual polymeric complex[3,9] decomposed at about 200 °C. DTA curve also showed three endotherms at temperatures corresponding to the above reactions. $La(AA)_3(H_2O)_2$ also showed similar DTA and TGA curves.

Pyridine adducts $Ln(AA)_3(Py)(H_2O)_2$ showed three DTA endotherms. One mole each of water and pyridine was released at about 80 °C forming monohydrates, then at about 120 °C one-half mole of acetylacetone was liberated from the monohydrates. Liberated water, pyridine and acetylacetone upon pyrolysis were identified by gas-chromatographic analysis.

$Ln(AA)_3(en)$ and $Ln(AA)_3(pn)$ showed irreversible pyrolytic DTA endotherms and subsequent exotherms in the range 130—160 °C. $Ln(AA)_3(ipa)$ also decomposed at 123—124 °C, accompanied by weight loss corresponding to the elimination of isopropanolamine.

15) W. H. Watson, R. J. Williams, and N. R. Stemple, *J. Inorg. Nucl. Chem.*, **34**, 501 (1972).

16) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

17) W. D. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, *ibid.*, **93**, 5258 (1971).

Table 5. DTA and TGA data of base adducts

Compound	Peak temp. (°C) on DTA curve		
	Weight loss (%) on TGA curve at corresponding peak temp.[a]		
$Nd(AA)_{33}(H_2O)_2$	68	110	207
	4.0 (3.8)[d]	15.0 (14.3)[e]	22
$La(AA)_3(H_2O)_2$	100	116_{sh}	184
	10	14.5 (14.4)[e]	16
$Nd(AA)_3(Py)(H_2O)_2$	81	118	208
	18.0 (17.4)[f]	28.0 (26.4)[g]	33
$La(AA)_3(Py)(H_2O)_2$	80	116	186
	19.0 (17.7)[f]	29.0 (26.8)[g]	30
$Nd(AA)_3$(ipa)	70	124	
	0	14 (14.5)[j]	
$La(AA)_3$(ipa)	75	123	203
	0	15 (14.7)[j]	33 (34.3)[k]
$Nd(AA)_3$(en)		160	162.5[c]
		17.0 [p]	17.5[p]
$La(AA)_3$(en)		128	134[c]
		6.0 [p]	7.5[p]
$Nd(AA)_3$(pn)		161	166[c]
		15 (14.4)[h]	35 (33.8)[i]
$La(AA)_3$(pn)		159	162[c]
		21 (13.4)[h]	33 (31.0)[i]
$Nd(AA)_3$(2-dipy)		188	209
		25.0 (27.0)[l]	38.5 (43.8)[m]
$Nd(AA)_3$(4-dipy)		209	218
		32 [p]	41 (43.8)[n]
$Nd(AA)_3$(phen)		229	246
		29.0 (29.2)[o]	34.0[p]
$La(AA)_3$(phen)		209	224
		14.0 [p]	30.0 (29.5)[o]

a) Temperatures with superscript c) indicate exothermic peaks, those without endothermic peaks.
b) Numbers in parentheses indicate the calculated values of weight loss accompanied by the elimination of components shown by the following superscripts. d) H_2O, e) H_2O+0.5 acetylacetone, f) H_2O+pyridine, g) H_2O+pyridine+0.5 acetylacetone, h) propanediamine, i) propanediamine+acetylacetone, j) isopropanolamine, k) isopropanolamine+acetylacetone, l) dipyridyl, m) 2,2′-dipyridyl+acetylacetone, n) 4,4′-dipyridyl+acetylacetone, o) phenanthroline, p) values are only approximate due to the close succession of DTA peaks.

On the other hand, $Ln(AA)_3$(phen), $Nd(AA)_3$(2-dipy) and $Nd(AA)_3$(4-dipy) showed pyrolysis in the range 190—200 °C.

Thermal stability increased in the following order, hydrate and unidentate base adducts<bidentate primary amine and isopropanolamine adducts<bidentate heterocyclic nitrogen base adducts.

Ease with which acetylacetone evolves from the hydrates, could be ascribed to the structure of complexes in which acetylacetone moieties were so arranged that they react readily with hydrogen atom in a coordinated water, forming hydrogen bonding between the carbonyl oxygen and the water hydrogen atoms.[11,18] Such a hydrogen bonding should also exist in the primary amine adducts. The relatively high thermal stability of the addition complexes with the bases such as dipyridyl or 1,10-phenanthroline may be thus understood to be due to the absence of reactive hydrogen atoms.

18) T. S. Davis and J. P. Fackler, *Inorg. Chem.*, **5**, 242 (1966).