Syntheses of *N,N'*-Bis(1-acetonylethylidene)ethylenediamine Complexes of Rare Earth Perchlorates

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N,N'-Bis(1-acetonylethylidene)ethylenediamine(AEH_2) complexes were prepared by the reaction of hydrous rare earth perchlorates with AEH_2 in methanol. Elemental analysis, X-ray powder diffraction analysis, pH titration, IR and luminescence spectrometries indicated that the complexes of the lighter rare earths were $Ln(AEH_2)_4(ClO_4)_3$, where Ln are La, Pr, Nd, and Sm, while the complexes of the heavier rare earths were hydroxocomplexes, $Ln(AEH_2)_2(ClO_4)_2(OH)\cdot H_2O$, where Ln are Gd, Dy, and Er. Anhydrous gadolinium perchlorate was reacted with AEH_2 in methanol under anhydrous conditions to give $Gd(AEH_2)_4(ClO_4)_3$. It was possible that a water molecule played an important role in the complexation of rare earth perchlorates with AEH_2 in methanol. The formation of the hydroxocomplexes with AEH_2 was related to the low coordinating ability of the perchlorate ion and to the charge densities of the rare earth ions as well as to the basicity of AEH_2.

A number of the rare earth complexes with neutral ligands have been prepared in organic solvents to avoid the coordination of the water molecule.[1,2] In the case of highly basic ligands such as amines,[3,4] the complexes have been prepared under anhydrous conditions to prevent hydrolysis. The number of the given ligands attached to rare earth ions depends on the ionic radii of the rare earth ions and on the coordinating abilities of the anions.

N, N'-Bis(1-acetonylethylidene)ethylenediamine(AEH_2) complexes have previously been prepared from the hydrous rare earth salts, such as chlorides, nitrates, and thiocyanates, in ethanol[5] or in a methanol–acetone mixture,[6] while the AEH_2 complexes of rare earth perchlorates have not been reported. The present paper will deal with the preparation of the complexes obtained by the reaction of AEH_2 with hydrous rare earth perchlorates and anhydrous gadolinium perchlorate in methanol. The AEH_2 complexes of the lighter rare earth perchlorates include more ligand molecules attached to the metal ion than those[5,6] of the lighter rare earth salts. The complexes obtained from hydrous, heavier rare earth perchlorates were hydroxocomplexes. Scarcely no hydroxocomplexes with neutral ligands are found in the literature.

Experimental

Materials. Rare earth oxides of a 99.9% purity were obtained from the Shin-etsu Chem. Ind. Co., Ltd. The hydrous rare earth perchlorates were prepared by dissolving a known amount of oxide in dilute perchloric acid and by then evaporating the mixture carefully on a hot plate. Anhydrous gadolinium perchlorate was obtained by heating the hydrate slowly up to 250 °C *in vacuo*.[3] The AEH_2 was prepared by the method shown in the literature.[7]

Preparation of Complexes Using Hydrous Rare Earth Perchlorates. The complexes were prepared by adding 10 ml of methanol containing an appropriate amount of AEH_2 (7 mM or 14 mM) to 15 ml of a methanol solution of rare earth perchlorate (3 mM). Lanthanum and praseodymium complexes were precipitated immediately. In the case of the other rare earths, the mixed solution was stirred for a few minutes and then allowed to stand overnight at room temperature to precipitate crystalline complexes.

Preparation of a Complex Using Anhydrous Gadolinium Perchlorate. The procedure was carried out in a dry nitrogen atmosphere. Anhydrous gadolinium perchlorate (*ca.* 3 mM) was dissolved in 15 ml of methanol, and then a small amount of the insoluble residue was filtered off. The filtrate was added to 10 ml of methanol including 14 mM of AEH_2, and the mixture was allowed to stand overnight at room temperature to give a crystalline product.

All the products were filtered, washed with methanol, and then dried *in vacuo*.

Elemental Analysis. A known amount of the complex was dissolved in dilute hydrochloric acid. The rare earth elements were determined gravimetrically.[8] The perchlorate ion was determined spectrophotometrically.[9]

Measurements. The IR spectra were recorded with a Perkin-Elmer 225 and a Hitachi EPI-L spectrophotometer. X-ray powder diffraction patterns were obtained with a Rigaku Denki diffractometer "Geiger-flex", using Ni-filtered Cu*Kα* radiation. The luminescence spectra of the complexes and AEH_2 in the solid state excited at 260 nm were measured with a Hitachi MPF model 3 spectrophotometer. The pH was measured by a Hitachi-Horiba F-7 pH meter.

Results and Discussion

The analytical data listed in Table 1 indicate that the complexes obtained may be classified into two types—the 'D' type[6] including the complexes obtained from the hydrous, lighter rare earth (La, Pr, Nd, and Sm) and anhydrous gadolinium perchlorates, and the 'E' type including the complexes obtained from the hydrous, heavier rare earth (Gd, Dy, and Er) perchlorates. The formulas are estimated to be $Ln(AEH_2)_4(ClO_4)_3$ for the 'D' type and $Ln(AEH_2)_2(ClO_4)_2(OH)\cdot H_2O$ for the 'E' type on the basis of the analytical data and the data to be described hereinafter. The X-ray diffraction spectra shown in Fig. 1 also support the above classification into two types.

The pH titration curves for the two types of complexes are compared in Fig. 2. The pH value of the aqueous solution of the praseodymium complex (the 'D' type) varied little from the initial pH value upon the addition of a standard acid solution. On the other hand, the titration curve of the erbium complex (the 'E' type) shows a pH break which corresponds to *ca.* one equivalence of the acid. When the titration was continued, the pH titration curves of both 'D'- and

TABLE 1. ANALYTICAL DATA OF COMPLEXES (%)

Ln	Type[a)		Ln	C	H	N	ClO_4
La	D	Found	10.5	42.93	6.04	8.21	22.0
		Calcd	10.4	43.22	6.00	8.40	22.4
Pr	D	Found	10.7	43.80	6.24	8.51	
		Calcd	10.5	43.16	5.99	8.39	22.3
Nd	D	Found	10.9	42.77	6.12	8.20	22.8
		Calcd	10.8	43.05	5.97	8.37	22.3
Sm	D	Found	11.4	42.08	5.90	8.10	
		Calcd	11.2	42.85	5.95	8.33	22.2
Gd[b)	D	Found	11.7	41.60	5.89	8.15	
		Calcd	11.6	42.61	5.97	8.28	22.1
Gd	E	Found	18.9	33.82	5.33	6.70	23.2
		Calcd	18.7	34.30	5.24	6.67	23.7
Dy	E	Found	19.4	33.71	5.01	6.24	
		Calcd	19.2	34.08	5.20	6.63	23.5
Er	E	Found	19.8	33.70	5.20	6.44	23.1
		Calcd	19.7	33.80	5.17	6.59	23.4

a) 'D' type: $Ln(AEH_2)_4(ClO_4)_3$, 'E' type: $Ln(AEH_2)_2(ClO_4)_2(OH)\cdot H_2O$. b) Complex was prepared from anhydrous gadolinium perchlorate. Other complexes were prepared from hydrous rare earth perchlorates.

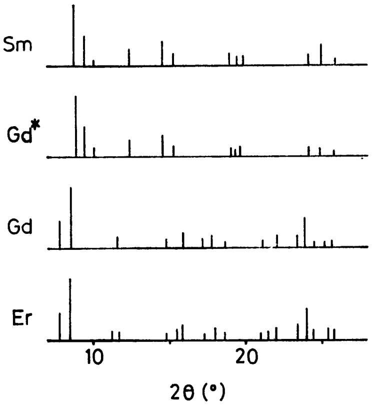

Fig. 1. X-ray powder diffraction diagrams of complexes. * Complex was prepared from anhydrous gadolinium perchlorate. The other complexes were prepared from hydrous rare-earth perchlorates.

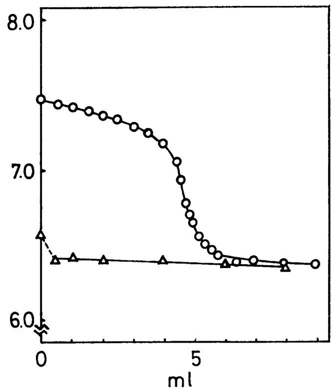

Fig. 2. Titration curves of complexes with 0.012 M HCl. —△—: Pr complex ('D' type), —○—: Er complex ('E' type).

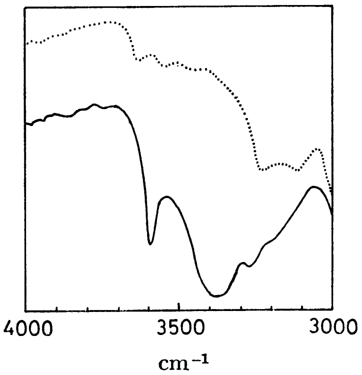

Fig. 3. Infrared spectra of gadolinium complexes in the OH and NH stretching region.
---------: 'D' type, ———: 'E' type

'E' types leveled off at a pH value of *ca.* 6.4. An odor of acetylacetone was also detected; it seems to be caused by a decomposition of AEH_2 into acetylacetone and diazepine.[10,11] The results of the pH titration are considered to indicate that 'E'-type complexes contain a hydroxyl group.

The presence of the hydroxyl group in the 'E'-type complexes is also suggested by the IR absorption spectra. The IR absorption spectra of gadolinium complexes in the 3000—4000 cm^{-1} region are shown in Fig. 3. For the 'E'-type complex of gadolinium, a sharp band is observed at 3594 cm^{-1}. The corresponding bands are also observed at 3596 cm^{-1} for the dysprosium complex and at 3600 cm^{-1} for the erbium complex. These sharp bands are assignable to the OH stretching of the hydroxyl group. In other reports, a similar assignment has been made for the sharp absorption bands of the rare earth hydroxo-compounds, *e.g.*, at 3600—3610 cm^{-1} (hydroxides),[12] 3585—3620 cm^{-1} (hydroxo-oxides),[12] 3425—3550 cm^{-1} (hydroxocarbonates)[13] and 3588 cm^{-1} (neodymium azide).[14] The broad band at 3380 cm^{-1} of the 'E' type might arise from the OH stretching vibration of the inherent water of the complex.[15,16] On the other hand, the 'D'-type complex of gadolinium shows no absorption bands due to hydroxyl and water molecule.

In Fig. 3, the broad band at 3100—3300 cm^{-1} observed in both 'D'- and 'E'-type complexes indicates that hydrogen-bonded O–H···N or O···H–N groups are present in the complexes.[5,17] The IR absorption bands of the complexes in the region of the C=O, C=N, and C=C stretching vibrations[17] are summarized in Table 2. In the case of the thorium(IV) complex[18]

TABLE 2. CHARACTERISTIC INFRARED ABSORPTION BANDS (cm^{-1}) OF COMPLEXES AND LIGAND

Ln	Type	(C=O)		(C=C) or (C=N)	
La	D	1605 s	1593 sh	1542 s	1496 m
Pr	D	1605 s	1592 sh	1542 s	1495 m
Nd	D	1605 s	1595 s	1540 s	1495 m
Sm	D	1606 s	1592 s	1542 s	1493 m
Gd	D	1606 s	1590 s	1547 s	1498 m
Gd	E	1594 s		1550 s	1495 m
Dy	E	1597 s		1550 s	1499 m
Er	E	1596 s		1550 s	1495 m
Ligand		1610 s		1582 s	1565 m
				1550 m	1520 s

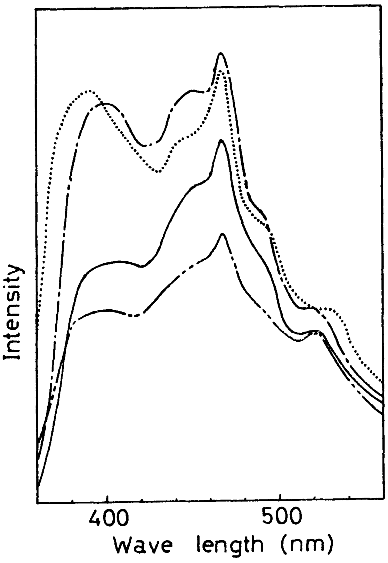

Fig. 4. Luminescence spectra of gadolinium complexes and AEH_2.
– – – – : 'C' type complex, – – – : 'D' type complex, ———: 'E' type complex, ---------: AEH_2.

containing both neutral and ionic ligands, $Th(AEH_2)(AE)(NO_3)_2$, the absorption intensity of $\nu_{(C=O)}$ at 1600 cm^{-1} is rather weaker than those of $\nu_{(C=N)}$ and $\nu_{(C=C)}$. Since the absorption bands $\nu_{(C=O)}$ of both 'D'- and 'E'-type complexes are very strong, these complexes seem not to contain an ionic ligand such as AEH^- or AE^{2-}.

Furthermore, the luminescence spectra in the solid state of AEH_2 and three gadolinium complexes with AEH_2 were recorded in the 360—560 nm range. The results are shown in Fig. 4. The fluorescence of the terpositive gadolinium ion could not be observed in the visible region because of the ^6P level of Gd^{3+} being in the ultraviolet region (—32 kK).[19] The luminescence spectra of the three gadolinium complexes are quite similar to that of AEH_2. The close similarity in the luminescence spectra suggests that the ligand molecules in the 'D'- and 'E'-type complexes of gadolinium are neutral, as are those in the 'C'-type complex of gadolinium.

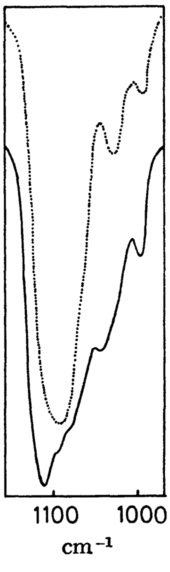

Fig. 5. Infrared spectra of complexes in the region of perchlorate absorption.
------: Pr complex ('D' type), ——: Dy complex ('E' type).

In Table 2, the $\nu_{(C=O)}$ bands of the 'D'-type complexes are found to split weakly into two peaks; this is not observed for the 'A'-, 'B'-, 'C'-, and 'E'-type complexes. The splitting suggests that the ligands in the 'D'-type complexes are coordinated and/or not coordinated with oxygen atoms.[20]

Figure 5 presents the IR absorption spectra assigned to perchlorate ions in the praseodymium and dysprosium complexes. The praseodymium complex shows two peaks in the 1100 cm^{-1} region. The perchlorate ion in the 'E'-type complexes appears to be coordinated weakly with the rare earth ions.[21]

TABLE 3. METAL-LIGAND STRETCHING VIBRATIONS (cm^{-1})

Type	La	Pr	Nd	Sm	Gd	Dy	Er
D	418	418	418	422	422		
E					429	430	432

The bands assignable to the metal-ligand stretching vibrations[6] are listed in Table 3. The absorption frequencies of these bands increase in the order of the atomic numbers of the rare earths.

The number of the ligand molecules attached to a metal ion in the 'D'-type complexes is more than those of the AEH_2 complexes of the other lighter rare earth salts, such as chlorides, nitrates, and thiocyanates.[5] The increasing of the ligand molecules is probably due to the low coordinating ability of the perchlorate ion.[2]

Gadolinium perchlorate forms a 'D'-type complex under anhydrous conditions, while it forms an 'E'-type complex under hydrous conditions. Therefore, it is obvious that a water molecule plays an important role in the formation of hydroxo complexes ('E' type). Since the hydroxo complexes with AEH_2 are obtained only from the hydrous, heavier rare earth perchlorates, the increase in the charge densities of rare earth ions and the low coordinating ability of the perchlorate ion are considered to result from the formation of the hydroxide ion. The hydroxide ion, which has a strong tendency to coordinate toward rare earth ions,[2] seems to be produced from a water molecule in the complex cation of heavier rare earths, $[Ln(H_2O)_x(Solvent)_y]^{3+}$. Actually, the perchlorate ion is present in the outer coordination sphere, and the other anionic species are present in inner coordination sphere of rare earth ions in alcohol,[22,23] though the coordination of the perchlorate ion in the 'E'-type complexes can not be explained.

Consequently, it may be presumed that the formation of the hydroxo complexes ('E' type) is related to the low coordinating ability of the perchlorate ion and the charge densities of the rare earth ions as well as to the basicity of AEH_2.

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