product. In the latter case, reaction 1 was pushed to completion by removing the hydrogen from the system. The LiAl phase was the only product observed. In both the partial decomposition product of $LiAlH_4$ and the admixture, the X-ray pattern for aluminum was observed but not that for LiH. A possible reason for the absence of the LiH pattern is the low diffracting power of the atoms in LiH resulting from their low atomic numbers. In the presence of aluminum, which absorbs part of the X-ray beam, the LiH lines may be too weak to observe.

It is observed in Figure 1 that a plot of log (pressure) *vs.* reciprocal temperature is linear. The following standard equation can, therefore, be used to obtain thermodynamic information on reaction 1

$$\ln P = (\Delta S/R) - (\Delta H/RT) \tag{2}$$

The thermodynamic data obtained on each sample are summarized in Table I. Similar data were obtained on admixtures of LiH and Al and on the partial decomposition product of $LiAlH_4$. The heat absorbed in reaction 1 is 19.2 ± 1 kcal/mol of H_2. The entropy change in the reaction is 28.6 ± 1 cal/deg mol of H_2. The large positive entropy change results primarily from the production of hydrogen gas.

TABLE I
HEAT AND ENTROPY CHANGES FOR REACTION 1
CALCULATED FROM THE EXPERIMENTAL DATA

Sample designation	Initial composition	ΔH, kcal/mol of H_2	ΔS, cal/deg mol of H_2
A	0.46 g of LiH + 1.54 g of Al	19.4	28.7
B	0.35 g of LiH + 1.16 g of Al	19.5	29.2
C	0.23 g of LiH + 0.77 g of Al	18.6	27.6
D	0.26 g of LiH + 1.74 g of Al	19.7	29.2
E	2.00 g of $LiAlH_4$	19.0	28.4
F	1.50 g of $LiAlH_4$	19.2	28.8
G	1.17 g of $LiAlH_4$ + 0.83 g of Al	18.8	28.1

Information on the heat of formation of the LiAl phase can be obtained from the data. For this purpose, it is useful to rewrite reaction 1 in terms of the atomic compositions of the phases.[8,9]

$$2LiH + 3.14Al_{0.90}Li_{0.10} = 2.57Al_{1.10}Li_{0.90} + H_2 \tag{1'}$$

The heat of formation of LiH at about 500° can be calculated from its known heat of formation at 298°, −21.50 ± 0.5 kcal/g-atom of Li. This is the average of two measured values.[10,11] The heat of formation of LiH at 500° from liquid lithium and gaseous hydrogen is calculated to be −22.1 ± 1 kcal/g-atom of Li using specific heat data on LiH,[12,13] Li,[14] and hydrogen[14] and the heat of fusion of Li.[14] Using this value in reaction 1′, the heat of the reaction

$$1.57Al_{0.90}Li_{0.10}(s) + Li(l) = 1.29Al_{1.10}Li_{0.90} \tag{3}$$

at about 500° is −12.6 ± 1 kcal/g-atom of Li. The reported heat of formation of LiAl,[15] −13.0 ± 4 kcal/g-atom of Li at 298°, is in good agreement with this value. It is also similar to the heats of formation of LiPb, LiCd, LiTl, and LiSn[15] which are, respectively, −14.6, −12.0, −12.8, and −16.8 kcal/g-atom of Li, respectively.

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Studies on the "Isomeric" Forms of Some β-Diketone Complexes of Europium(III) and Neodymium(III)[1]

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The coordination chemistry of rare earth elements has been investigated by a large number of researchers and extensive reviews have been published.[3–5] One important result of this work was the discovery that certain complexes of europium(III) are promising as laser materials.[6] Two compounds whose fluorescence spectra have received considerable attention[7–10] and which have shown laser action in alcohol solution are piperidinium tetrakis(1,3-diphenyl-1,3-propanediono)europate(III) and piperidinium tetrakis(1-phenyl-1,3-butanediono)europate(III). The anionic ligand moieties are also called dibenzoylmethanate and benzoylacetonate and the compounds are abbreviated as $[Pip][Eu(DBM)_4]$ and $[Pip][Eu(BA)_4]$, respectively.

Bauer, Blanc, and Ross[8] reported these two compounds and the Gd analog with DBM each to have two

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modifications, designated α and β, which have significantly different fluorescence spectra in the solid state but whose elemental chemical analyses were regarded to indicate chemical identity. By analysis of the allowed transitions for various molecular symmetries and comparison with the observed spectra they concluded that the α and β forms were stereoisomers of different symmetries. In the case of [Pip][Eu(DBM)$_4$], a change in the 6100-Å region of the fluorescence spectrum from three lines for the α form to two lines for the β form was said to indicate a change in symmetry from D_{2d} to S_4. This isomerization could be effected by recrystallization from absolute methanol. It was also noted that addition of dimethylformamide (DMF) to the alcohol solution caused it to yield a two-line spectrum[11] resembling that of the β form. For [Pip][Eu(BA)$_4$] the fluorescence spectrum in the 6100-Å region showed only two lines but these had different spacings for the two isomers; this was interpreted as an isomerization of the structure from D_{2d} to C_{4v} or C_4 symmetry.

We felt that it would be of interest to isolate each of the isomeric forms reported, further characterize them chemically, and, if they were chemically identical, examine the physical differences which could result in different spectra.

TABLE I

ELEMENTAL ANALYSES

Compound	Empirical formula	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
α-[Pip][Eu(DBM)$_4$][a]	$C_{65}H_{56}NEuO_8$	69.02	4.99	1.24	69.42	4.83	1.29
β-[Pip][Eu(DBM)$_4$]·H$_2$O[a]	$C_{65}H_{58}NEuO_9$	67.94	5.09	1.22	67.94	5.10	1.18
β-[Pip][Eu(DBM)$_4$]·DMF	$C_{68}H_{63}N_2EuO_9$	67.82	5.27	2.33	67.98	5.32	2.26
α-[Pip][Eu(BA)$_4$]	$C_{45}H_{48}NEuO_8$	61.22	5.48	1.59	61.53	4.84	2.02
α-[Pip][Nd(BA)$_4$][b]	$C_{45}H_{48}NNdO_8$	61.76	5.53	1.60	62.08	5.42	1.94
β-[Pip][Nd(BA)$_4$]·H$_2$O[b]	$C_{45}H_{50}NNdO_9$	60.52	5.64	1.57	60.14	5.55	2.03

[a] Water content determined by Karl Fischer titration method: α, 0.12%; β, 2.0%. Calcd for 1 mol of water: 1.6%. [b] The neodymium compounds were found by X-ray powder methods to be isomorphous with the corresponding europium compounds.

TABLE II

CRYSTALLOGRAPHIC DATA

Compound	Unit cell[a] dimensions a, Å	b, Å	c, Å	β	Density, g cm^{-3}	Z	Space group
α-[Pip][Eu(DBM)$_4$]	24.0	23.8	19.4	90° 25′	1.36	8	C2/c or Cc
β-[Pip][Eu(DBM)$_4$]·H$_2$O	18.93	18.75	16.18	92° 42′	1.31	4	P2$_1$/n
β-[Pip][Eu(DBM)$_4$]·DMF	29.2	9.38	28.6	128° 42′	1.31	4	C2/c or Cc
α-[Pip][Eu(BA)$_4$]	11.91	19.71	19.06	110° 43′	1.40	4	P2$_1$/c

[a] All crystals are monoclinic. The dimensions are accurate to about 0.5%.

Experimental Section

Preparation of Compounds.—The method of Bauer, *et al.*[8] in which piperidine was added to an alcohol solution of the chelate and the rare earth chloride, was used to prepare the α and β modifications of [Pip][Eu(DBM)$_4$], [Pip][Eu(BA)$_4$], and [Pip][Nd(BA)$_4$]. Benzoylacetone and dibenzoylmethane were obtained from Distillation Products Industries, hydrated europium trichloride was from American Potash and Chemicals Corp. (99.9% pure), neodymium oxide was from Kleber Laboratories, Inc. (99.9% pure), and piperidine was reagent grade from Matheson Coleman and Bell. The hydrated europium trichloride was dissolved in absolute methanol or absolute ethanol or it was dehydrated with 2,2-dimethoxypropane before addition of the ligand, with the same resultant product each time. The initial product was recrystallized in each case from methanol or butanol. Rapid crystallization produced the β form which, if left standing, redissolved in the recrystallization liquor and the α form slowly formed. The DMF adduct of [Pip][Eu(DBM)$_4$] was obtained by recrystallization from methanol to which some DMF had been added.

Analyses for C, N, and H were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and water analyses by Karl Fischer titrations were carried out by the ORNL Analytical Chemistry Division. The results of these analyses are given in Table I.

Physical Measurements.—Infrared spectra were obained from Nujol mulls on a Perkin-Elmer 337 infrared spectrometer. Fluorescence spectra were recorded with an Aminco-Bowman spectrophotofluorometer. X-Ray diffraction data were taken by standard powder and precession camera methods.

Results and Discussion

The α and β "isomers" of both β-diketone complexes were prepared and found to correspond to those previously reported by Bauer, *et al.*,[8] both in the physical appearance of the crystals and in their fluorescence spectra. In each case it was determined by elemental analysis that the β form contains one molecule of water per molecule of complex. This observation was corroborated by the infrared spectra of the β forms which showed the characteristic O–H stretching modes as a broad band at 3740 cm^{-1}; this band was absent for the α forms. Analyses also showed that the crystals from the solution containing DMF are an adduct containing one molecule of DMF per molecule of complex.

The hydrated form tends to lose water on standing and become the anhydrous form. Because this was a problem in studying the BA complex of Eu, the Nd complex was also prepared in an effort to get more stable crystals. A successful elemental analysis of [Pip][Nd(BA)$_4$]·H$_2$O was obtained, and it was shown by X-ray powder methods to be isomorphous with [Pip][Eu(BA)$_4$]·H$_2$O.

Single crystals of the anhydrous forms and the DMF adduct were readily obtained for X-ray study, but crystals of the hydrates were always quite small although

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repeated attempts were made to grow larger ones. Crystallographic data from single-crystal studies are given in Table II for those compounds for which suitable crystals could be grown. From these data it is seen that no higher symmetry for the chelated Eu than S_2 or C_2 is required by any of these crystal structures, although a higher symmetry is not ruled out. The important question of whether the water and/or the DMF is involved in the coordination sphere of the Eu ion or is just a "lattice" molecule must await crystal structure determinations.

In summary, our results show that the differences in the fluorescence spectra can be attributed to the different crystal structures and presumably different Eu environments caused by the presence of H_2O or DMF and that it is not necessary to assume the existence of stereoisomers. They also serve to emphasize the point made by previous authors regarding the necessity of careful chemical identification of the species from which interpretations of the spectra are to be made.

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Syntheses of *cis*- and *trans*-Tetraamminebis(pyridine)ruthenium(II). High Stereospecificity in Ruthenium(II) Substitution Reactions

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Recent efforts in this laboratory have been directed toward elucidation of substitution mechanisms in ruthenium(II)–ammine complexes. In the course of this work, it became necessary to distinguish between the stereochemical isomers of tetraammineruthenium complexes, $Ru^{II}(NH_3)_4X_2$ (A), where X is either H_2O or Cl^-. Reaction of either *cis*-A or *trans*-A with excess pyridine gives a single isomer of $Ru(NH_3)_4(py)_2^{2+}$ in each case, presumably identical in stereochemistry with the initial complex. The two ions $Ru(NH_3)_4(py)_2^{2+}$ thus prepared are distinguished by differences in their cation-exchange elution behavior and by differences in the position, shape, and intensity of absorption bands in the visible spectrum.

Experimental Section

All reactions were carried out at ambient temperature unless otherwise noted.

***trans*- and *cis*-[Ru(NH$_3$)$_4$(py)$_2$][ClO$_4$]$_2$.**—Synthesis was accomplished from the respective dichlorotetraammineruthenium(III) salt by a procedure analogous to one used to prepare pentaammineruthenium(II) complexes of aromatic heterocycles from $[Ru(NH_3)_5Cl]Cl_2$.[2] *trans*-$[Ru(NH_3)_4Cl_2]Cl$[3] (0.063 g, 2.3×10^{-4} mol) was dissolved in 5 ml of pyridine hydrochloride buffer ([py] ≈ 1 *M*) and deaerated with a stream of purified argon. Granular amalgamated zinc (0.5 g) was added, and after stirring for 20 min, the resulting yellow solution was filtered. Addition of sodium perchlorate gave 0.099 g (82% crude yield) of $[Ru(NH_3)_4(py)_2][ClO_4]_2$. Recrystallization from aqueous methanol gave 0.067 g (56% over-all yield) of the yellow salt. *Anal.* Calcd for $RuC_{10}H_{22}O_8N_6Cl_2$: C, 22.8; H, 4.2; N, 16.0. Found: C, 22.9; H, 4.5; N, 16.2.

A similar procedure starting with *cis*-$[Ru(NH_3)_4Cl_2]Cl$[3] (0.103 g, 3.7×10^{-4} mol) gave the crystalline yellow solid *cis*-$[Ru(NH_3)_4(py)_2][ClO_4]_2$ (0.065 g, 33% yield when recrystallized). *Anal.* Calcd for $RuC_{10}H_{22}O_8N_6Cl_2$: C, 22.8; H, 4.2; N, 16.0. Found: C, 22.5; H, 4.4; N, 16.6. Analyses of this compound gave poor reproducibility owing to consistent detonation during combustion.

Cation-Exchange Analysis of Reaction Mixtures.—Reaction mixtures containing $Ru(NH_3)_4(py)_2^{2+}$ and other species generated by one of the procedures described below were quenched with acidic hydrogen peroxide and then were eluted from a cation-exchange resin column (11.5-cm length, Biorad AG5OW-X2), with acidic sodium chloride solution (pH 1). Sodium ion concentration in the eluent was gradually increased from an initial 0.3 *M* to a final 3.3 *M*. Aliquots of 10 ml each were collected and their uv spectra were recorded. This procedure was tested with a solution of the known ion $Ru(NH_3)_5py^{2+}$. Oxidation with acidic H_2O_2 followed by cation exchange leads to separation of an elution band containing a quantitative yield of the known Ru(III) analog,[2] $Ru(NH_3)_5py^{3+}$. The ions *cis*- and *trans*-$Ru(NH_3)_4py_2^{3+}$ were the only +3 ruthenium species detected in mixtures from methods A and B. These eluted at the approximate sodium ion concentrations 2.2 and 2.5 *M*, respectively, and were cleanly separated on the column from other reaction components and from each other. The separation of $Ru(NH_3)_5py^{3+}$ from *cis*-$Ru(NH_3)_4(py)_2^{3+}$ in the elution of products from method C is poor. However, an estimate of the percentage of each can be made because of spectra differences.

The three methods used to generate $Ru(NH_3)_4(py)_2^{2+}$ solutions for analysis by ion exchange follow. (A) A 3.2-mg (1.2×10^{-5} mol) sample of either *cis*- or *trans*-$[Ru(NH_3)_4Cl_2]Cl$ was dissolved in 10 ml of pyridine hydrochloride buffer solution ([py] ≈ 1 *M*) and the solution was deaerated with purified argon. Amalgamated zinc (0.5 g) was added, and the reaction mixture was stirred in the dark for 30 min and then quenched. (B) A 3.2-mg (1.2×10^{-5} mol) sample of either *cis*- or *trans*-$[Ru(NH_3)_4Cl_2]Cl$ was dissolved in 10 ml of the pyridine buffer and the solution was deaerated. To this solution was added *via* syringe techniques 1.0 ml of Cr(II) solution ([Cr(II)] = 0.019 *M*), and the reaction mixture was stirred in the dark for 30 min and then quenched. (C) A 5.3-mg sample of $[Ru(NH_3)_5py][ClO_4]_2$ was dissolved in 10 ml of the pyridine buffer solution and deaerated. Zinc (0.5 g) was added, and the solution was stirred in the dark for 2.5 hr at 60° and then quenched.

Results and Discussion

Amalgamated zinc reduction of *trans*-$[Ru(NH_3)_4Cl_2]Cl$ in pyridine buffer gives a bright yellow solution from which can be isolated $[Ru(NH_3)_4(py)_2][ClO_4]_2$. The solution spectrum of this material has an intense absorption band centered at 423 nm. Similar treatment of *cis*-$[Ru(NH_3)_4Cl_2]Cl$ gives a solid with the correct analysis for $[Ru(NH_3)_4(py)_2][ClO_4]_2$ but with a different spectrum (λ_{max} 410 nm, shoulder at 375 nm; see Table I). Oxidation of either product followed by elution from a cation-exchange column gave a single ruthenium(III) component. An equal mixture of the two submitted to the same treatment elutes as two cleanly separated bands suggesting that the products of the syntheses are stereochemically pure and have

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