absolute ethanol, and $ZnCO_3$ (1.7 g, 0.014 mole) was added to the warm solution. The reaction mixture was refluxed with stirring for a 6–8-hr period and then filtered to remove any unreacted carbonate. The filtrate was cooled down to 0° until a product crystallized; this generally happened after cooling overnight. The solid was filtered, washed with ethanol, and then allowed to dry in air; yield, 1.8 g; mp 104°. Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of the mother liquor. The compound is soluble in benzene, carbon tetrachloride, and chloroform and insoluble in cold water.

Anal. Calcd mol wt for $Zn_4O((C_4H_9)_2PSO)_6$: 1437.0. Found (0.86, 1.00, 2.05 g/100 ml): 1387, 1428, 1443. Calcd neut equiv: 718.5. Found: 710.9, 720.1. Calcd for $Zn_4C_{48}H_{108}P_6S_6O_7$: Zn, 18.19; C, 40.11; H, 7.57. Found: Zn, 18.02; C, 41.14; H, 7.88.

Preparation of Basic Zinc Diethylphosphinothioate.—The same procedure given for the *n*-butyl derivative, using $(C_2H_5)_2PSOH$ (0.99 g, 0.007 mole) and $ZnCO_3$ (0.6 g, 0.005 mole), yielded 0.4 g of product, mp 273°. The compound is soluble in benzene, carbon tetrachloride, and chloroform and is insoluble in cold water.

Anal. Calcd mol wt for $Zn_4O((C_2H_5)_2PSO)_6$: 1100.4. Found (0.80, 1.30, 2.00 g/100 ml): 1052, 1030, 1081. Calcd neut equiv: 550.19. Found: 554.8, 540.4. Calcd for $Zn_4C_{24}H_{60}P_6S_6O_7$: Zn, 23.76; C, 26.19; H, 5.49. Found: Zn, 23.70; C, 25.60; H, 5.20.

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Clarification of Discrepancies in the Characterization of Lanthanum Series Complexes of 2,2,6,6-Tetramethyl-3,5-heptanedione

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Large discrepancies have been observed in the properties of lanthanum series chelates with the anion of 2,2,6,6-tetramethyl-3,5-heptanedione prepared by the methods of Hammond, *et al.*,[1] and Eisentraut and Sievers.[2] We have repeated the synthesis of the Er(thd)$_3$ complex[3] using both procedures. The product isolated using the Hammond method is an adduct with N,N-dimethylformamide, DMF, and the one isolated from the procedure in ref 2, an unsolvated complex with the formula Ln(thd)$_3$. DMF adducts resulted also when the unsolvated chelates were recrystallized from DMF. These Ln(thd)$_3$·DMF adducts have the properties of the products obtained by Hammond. Table I lists the melting points of complexes prepared by the various methods.

TABLE I

MELTING POINTS OF LANTHANUM SERIES COMPLEXES PREPARED BY VARIOUS PROCEDURES

Metal	Mp,[2] °C	Mp,[1] °C	Mp, °C, DMF adducts, this work[b]
Er	179–181	153–154	153–154
Sm	195.5–198.5	143–144	146.5–147.5
Ho	180–182.5	154–155	151.5–154.5
La	238–248[a]	148–149	118–235[c]

[a] Melting point taken in a sealed, evacuated tube. [b] Prepared by recrystallization of the Ln(thd)$_3$ complexes from DMF as described in the Experimental Section. A second sample of the Er(thd)$_3$·DMF adduct was prepared by the method in ref 1; this sample melted within 2° of the value in the table. [c] The melting point of this adduct depended upon the length of time it was exposed to air for removal of excess DMF.

The Ln(thd)$_3$·DMF adducts have not been recognized in the literature, although another DMF adduct of a rare earth β-diketonate, namely, tris(dibenzoylmethanato)(N,N-dimethylformamide)europium(III),[4] has been characterized. Other claims for the existence of thd complexes of various types have also been reported.[5,6] However, adducts of the type Ln(β-diketonate)$_3$·L, where L is a mono- or bidentate ligand with oxygen or nitrogen as the donor, are not uncommon.[4,7–10]

Experimental Section

The preparative methods described in ref 1 and 2 were followed closely to obtain products with properties matching those described in the earlier papers. The Ln(thd)$_3$·DMF adducts were prepared by recrystallization of the unsolvated complexes from hot DMF. The excess DMF was removed using a water aspirator to pull air through a sintered funnel containing the solid for 4 or 5 hr, followed by exposure to air overnight.

Thermogravimetric Analyses.—Ten-milligram samples were used in the Du Pont Model 950 thermogravimetric analyzer. The heating rate was set for 10°/min and the flow of dry helium, measured with a soap bubble flowmeter, was 60 cc/min.

Nmr Spectra.—Proton nmr spectra of carbon tetrachloride solutions were obtained with the Varian Associates Model A-60 spectrometer at the ambient probe temperature. The internal reference was tetramethylsilane.

Infrared Spectra.—The Perkin-Elmer Model 137B Infracord spectrophotometer was used for comparison of spectra for the products isolated from the various synthetic procedures. Samples in the form of mineral oil mulls were held between rock salt plates. Band positions in the 4000–600-cm^{-1} range were accurately measured with the Perkin-Elmer Model 521 grating infrared spectrophotometer for an 11% solution of DMF in CCl_4 and for saturated solutions of Er(thd)$_3$ and Er(thd)$_3$·DMF in CCl_4 using matched 0.025-mm liquid NaCl cells. Below 800 cm^{-1} both erbium complexes were also run as mineral oil mulls with rock salt plates, since C–Cl frequencies in CCl_4 absorbed strongly in some areas of this region.

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(3) The following abbreviations will be used: Ln = trivalent lanthanum series ions, and thd = the anion of 2,2,6,6-tetramethyl-3,5-heptanedione.

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TABLE II

ELEMENTAL ANALYSES OF DMF ADDUCTS OF TRIS(2,2,6,6-TETRAMETHYL-3,5-HEPTANEDIONATO)LANTHANUM SERIES COMPLEXES[a]

Complex	% theoretical				% experimental			
	Carbon	Hydrogen	Nitrogen	Metal	Carbon	Hydrogen	Nitrogen	Metal
Er(thd)$_3$·DMF[b]	54.72	8.16	1.77	21.17	54.71	8.27	1.98	21.33
Er(thd)$_3$·DMF[c]					54.85	8.27	1.78	20.92
Sm(thd)$_3$·DMF	55.92	8.34	1.81	19.44	55.91	8.47	1.85	19.14
Ho(thd)$_3$·DMF	54.88	8.19	1.78	20.93	54.94	8.26	1.80	20.66
La(thd)$_3$·DMF[d]	56.76	8.47	1.84	18.23	56.45	8.50	1.93	17.74
La(thd)$_3$·2DMF[e]	56.10	8.57	3.35	16.64	55.83	8.72	3.34	15.80

[a] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. [b] Prepared by recrystallization of unsolvated Er(thd)$_3$ from DMF. [c] Prepared by the method in ref 1. [d] Synthesized by vacuum recrystallization of unsolvated La(thd)$_3$ from degassed DMF. The excess DMF was removed by forcing air to pass through a sintered filter containing the product for 4 or 5 hr. [e] Prepared by recrystallization of unsolvated La(thd)$_3$ from DMF followed by removal of excess DMF with a stream of dry nitrogen for 72 hr, with the exclusion of air.

Results and Discussion

The large discrepancies in the melting points of the complexes isolated by Hammond, *et al.*, and by Eisentraut and Sievers, which were verified in this work, suggested that different compounds were formed. Further investigation for characterization and comparison of the complexes confirmed this suggestion. The experimental evidence which supports this conclusion is presented in the subsequent sections.

Elemental Analyses.—Analyses of the lanthanum series complexes shown in Table II were in good agreement with percentages calculated for adducts having the formula Ln(thd)$_3$·DMF. The analysis for the erbium complex which was prepared by Hammond's method is in agreement with the stoichiometry Er(thd)$_3$·DMF. The elemental analyses for the pure, unsolvated Ln(thd)$_3$ chelates are given in ref 2. In the case of the DMF adduct of the lanthanum complex, the analyses for two products prepared by somewhat different procedures reflect the uncertain composition of this species (see the discussion under Thermogravimetric Analyses).

Low values of molecular weight determinations for the DMF adducts in benzene and carbon tetrachloride indicate the possibility of partial dissociation in solution.

Thermogravimetric Analyses.—The thermogravimetric analyses, tga, of all Ln(thd)$_3$·DMF complexes indicated a definite loss in weight, beginning at 115–120° and ending at 150–155°, prior to the temperature at which sublimation commenced. On the other hand, thermograms of the unsolvated Ln(thd)$_3$ chelates showed no indication of a weight loss until the sample began to sublime.[11] Following the loss of DMF in the adducts, the tga curves were essentially superimposable with those for the unsolvated chelates. The percentage of the initial weight loss in DMF adducts corresponded approximately to that expected for a 1:1 stoichiometry.

For the DMF adduct of the lanthanum complex, the initial weight loss was variable and occurred at lower temperatures than that for the other adducts. One sample of this DMF adduct, prepared as described in the Experimental Section, except for being exposed to air 1 additional day, was examined periodically by tga and found to contain 14% DMF after the first 5-hr aspiration period, 10% DMF (∼1 mole) after exposing to air overnight, 6% following a second 5-hr aspiration period, and finally, 3% DMF at the conclusion of the second night of exposure to air. Owing to these data and the elemental analyses, the mole ratio of DMF to La(thd)$_3$ cannot be assigned with any degree of assurance.

Nmr Spectra.—The resonance positions for the methylene and *t*-butyl methyl protons in unsolvated La(thd)$_3$ are found at 5.68 and 1.08 ppm, respectively,[2] downfield from tetramethylsilane. The formyl and *cis*- and *trans*-methyl protons (with respect to the formyl hydrogen) in DMF dissolved in carbon tetrachloride are located at 7.85, 2.92, and 2.80 ppm, respectively. The spectrum of La(thd)$_3$·DMF with a 1:1 stoichiometry (see Table II) confirmed the presence of DMF. The DMF proton resonances in the adduct were shifted downfield from DMF in CCl$_4$ by 10 cps for the formyl proton, 1.5 cps for the *cis*-methyl proton, and 4.5 cps for the *trans*-methyl proton. These downfield shifts indicate that DMF functions as a donor in the adduct.[12] The retention of two methyl peaks in the spectra of DMF complexes with metal halides has been used as an argument for coordination by the carbonyl oxygen as opposed to the nitrogen.[13] The methylene proton resonance in the adduct was shifted upfield by 9 cps relative to that in La(thd)$_3$, while the *t*-butyl proton was unchanged. These data indicate clearly that a new complex is formed.

Infrared Spectra.—Examination of the infrared spectra of the unsolvated Ln(thd)$_3$ complexes and the DMF adducts revealed the presence of new absorption bands in the spectra of the adducts. Conclusions regarding the nature of the interaction between DMF and Er(thd)$_3$ are based on accurate measurement of band positions in the spectra of DMF, Er(thd)$_3$·DMF synthesized by Hammond's procedure,[1] and Er(thd)$_3$ prepared by the method of Eisentraut and Sievers.[2] The three spectra, listed below, give band positions in wavenumbers and include intensities specified by w = weak, m = medium, s = strong, and sh = shoulder.

Infrared spectrum of DMF: 2990 w, 2932 s, 2855 m,

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(11) K. J. Eisentraut and R. E. Sievers, *J. Inorg. Nucl. Chem.*, in press.

(12) E. S. Gore, D. J. Blears, and S. S. Danyluk, *Can. J. Chem.*, **43**, 2135 (1965).

(13) S. J. Kuhn and J. S. McIntyre, *ibid.*, **43**, 375 (1965).

2805 w, 2776 w, 2760 sh, 1950 w, 1728 m, 1686 s, 1681 s, 1502 m, 1487 sh, 1455 m, 1437 m, 1404 s, 1384 s, 1314 w, 1257 m, 1152 w, 1088 s, 1063 m, 865 w, and 657 s.

Infrared spectrum of $Er(thd)_3 \cdot DMF$: 2963 s, 2954 sh, 2929 sh, 2903 m, 2866 w, 2809 w, 1666 s, 1604 m, 1589 s, 1574 s, 1548 m, 1538 s, 1504 s, 1491 sh, 1478 m, 1459 sh, 1450 m, 1418 sh, 1414 s, 1403 s, 1385 s, 1357 s, 1284 w, 1244 w, 1225 m, 1195 m, 1177 w, 1140 m, 1102 w, 1085 sh, 1061 w, 1022 w, 960 w, 929 w, 869 m, 818 w, 719 w, 677 m, and 611 m. The bands at 791 m, 762 m, 755 m, and 735 m which were obscured in the spectrum of the sample dissolved in CCl_4 were observed in a mineral oil mull.

Infrared spectrum of $Er(thd)_3$: 2965 s, 2958 sh, 2932 sh, 2905 m, 2868 m, 1596 s, 1577 sh, 1571 s, 1567 sh, 1561 sh, 1555 sh, 1550 s, 1546 sh, 1537 sh, 1530 sh, 1522 sh, 1517 sh, 1509 s, 1502 s, 1493 sh, 1479 m, 1460 m, 1449 s, 1419 sh, 1406 s, 1401 s, 1388 s, 1357 s, 1300 sh, 1288 w, 1247 m, 1225 s, 1196 w, 1177 m, 1141 s, 1023 w, 961 w, 933 w, 929 w, 870 s, 720 m, and 611 m. The following bands, which were obscured in the CCl_4 solution, were observed in the spectrum of the sample run as a mineral oil mull: 819 w, 769 s, 765 s, 736 m, and 731 m.

New bands appearing in the $Er(thd)_3 \cdot DMF$ spectrum which are not found in the spectrum of $Er(thd)_3$ are located at 1666, 1102, 1061, and 677 cm^{-1}, and are apparently due to the presence of DMF in the adduct. The absorption band at 657 cm^{-1} in the DMF spectrum, attributed to an N—C═O bending frequency, was shifted to 677 cm^{-1} in $Er(thd)_3 \cdot DMF$. The shift of this band to higher frequencies has been observed in the spectra of complexes of DMF with metal halides.[14] The band in DMF located at 1088 cm^{-1} has been variously assigned and observed to shift mostly to higher frequencies in DMF adducts of metal halides.[15] That this band may have shifted to 1102 cm^{-1} in the $Er(thd)_3 \cdot DMF$ adduct is subject to question. The third absorption located at 1061 cm^{-1} in the adduct appears to originate from the unassigned 1063-cm^{-1} band in DMF.[16] Perhaps the most significant evidence for interaction between DMF and the erbium chelate is the shift of the carbonyl stretching frequency in DMF from 1686 to 1666 cm^{-1} in the $Er(thd)_3 \cdot DMF$ adduct. The shift of this absorption to lower frequencies in DMF adducts of metal halides[15,16] appears to be a reliable criterion upon which to choose coordination by DMF through oxygen rather than nitrogen. This conclusion is also supported by our nmr evidence. The exact nature of the complex cannot be specified with the information available; the DMF could either be bonded to the metal or to some electron-acceptor site in the ligand shell. An X-ray analysis or perhaps fluorescence measurements of the type reported in ref 4 should shed further light on this problem.

The experimental evidence presented in this study demonstrates conclusively that the complexes prepared using the method of Hammond, *et al.*, are adducts with the formula $Ln(thd)_3 \cdot DMF$ while those obtained by following the procedure suggested by Eisentraut and Sievers are unsolvated chelates with the formula $Ln(thd)_3$.

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Ionic Equilibria in Mixed Solvents. II. Hydrolysis of Beryllium Ion in a 0.1 Mole Fraction Dioxane–Water Mixture and in Aqueous Solution Containing 3 *M* $LiClO_4$ as an Ionic Medium

BY HITOSHI OHTAKI AND HIDEKI KATO

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The preceding paper of this series[1] described the hydrolytic reaction of beryllium ion in a 0.2 mole fraction dioxane–water mixture containing 3 M $LiClO_4$ as an ionic medium and concluded that $Be_3(OH)_3^{3+}$ was the predominant species in the solution in which beryllium ion hydrolyzed.

In the present study the hydrolytic reaction of beryllium ion was examined in different solvent systems such as a 0.1 mole fraction (35.21% w/w) dioxane–water mixture and an aqueous solution containing 3 M $LiClO_4$ as an ionic medium, and results obtained were compared with the previous findings. Symbols used in the present paper are the same as those used in part I.[1]

Method of Measurements

The method of measurements was essentially the same as that employed in part I of this series. In aqueous solutions with $B \leq 0.0050\ M$, a technique of coulometric generation of hydroxide ions in the forward titrations and of hydrogen ions in the back titrations was employed and no solutions were added from the burets to the test solution.

The emf of the cell used may be written, at 25°, as

$$E = E^\circ - 59.15 \log h + E_j(h, B)$$

assuming the constant activity coefficient of hydrogen ion. E° is a constant involving the activity coefficient. h and B represent concentrations (moles per liter) of hydrogen and beryllium ions, respectively. The liquid junction potential, $E_j(h, B)$, is experimen-

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