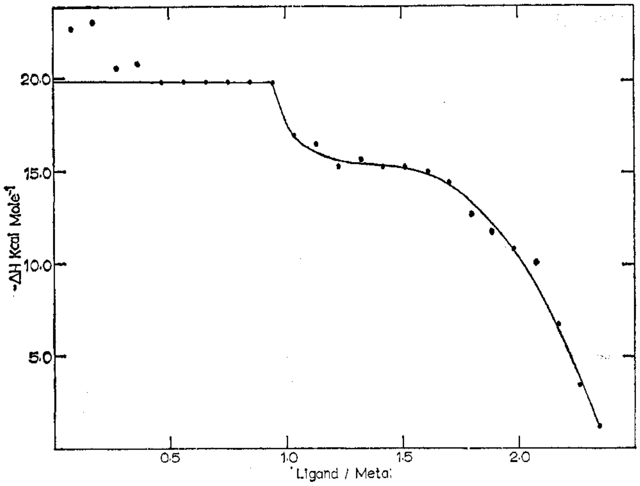

Figure 3.—Enthalpy curve for the formation of $Nd(dien)_n(NO_3)_3$.

metal ion is reflected in the lower enthalpy changes ($\Delta H_1 = -19.8$, $\Delta H_2 = -15.4$ kcal mol^{-1}) observed for neodymium nitrate compared with neodymium perchlorate (Table IV).

The total enthalpies of complexation, ΔH_c, for the formation of tetrakis-ethylenediamine chelates[13] and tris-diethylenetriamine chelates are given in Table V. The total enthalpy of complexation is less for the tris-diethylenetriamine chelates for each lanthanide ion, even though it involves formation of nine metal–nitrogen bonds compared to only eight for the tetrakis-ethylenediamine chelates. Furthermore, the difference in ΔH_c increases with decreasing metal ion radius, indicating the presence of greater steric repulsions in the tris-diethylenetriamine chelates. Since the nitrogen atoms in each of these ligands are expected to be of comparable donor strength, a comparison of ΔH_c values provides a quantitative measure of the difference in the steric requirements of these two ligands in high-coordinate complexes, as a function of metal ion radius.

TABLE V

TOTAL ENTHALPIES OF COMPLEXATION FOR ETHYLENEDIAMINE AND DIETHYLENETRIAMINE CHELATES OF LANTHANIDE PERCHLORATES

	Total enthalpy change, kcal mol^{-1}		
Ln^{3+}	$-\Delta H_c$(en)	$-\Delta H_c$(dien)	Difference
La^{3+}	57.6	56.7	0.9
Pr^{3+}	59.9	58.0	1.9
Nd^{3+}	60.4	58.0	2.4
Sm^{3+}	60.7	57.6	3.1
Gd^{3+}	60.9	57.5	3.4
Dy^{3+}	60.1	56.3	3.8
Er^{3+}	63.4	57.8	6.6
Yb^{3+}	66.1	56.2	9.9

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Preparation and Properties of Lanthanide Chelate Complexes

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Compounds of five types have been synthesized: $M(dpm)_3$ [M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu]; $M(dpm)_3py$ [M = same 12 metals]; $M(dpm)_3dipy$ [M = same first 11 metals, not Lu]; $M(dpm)_3phen$ [M = same first 11 metals, not Lu]; and $Ce(dpm)_4$ [where dpm = dipivaloylmethane, py = pyridine, dipy = α,α'-dipyridyl, phen = 1,10-phenanthroline]. They have been characterized by their thermal (melting point, dta, tga), spectral (ir, visible, uv), and magnetic (susceptibility, Weiss constant) properties and are under investigation as proton nmr shift reagents.

Introduction

The recently reported[1] discovery that the pyridine adduct of tris(dipivaloylmethanato)europium(III), $Eu(dpm)_3(py)_2$, could be used as a proton nmr shift reagent for cholesterol prompted us to begin the preparation of a series of analogous lanthanide complexes with the same bulky bidentate β-keto enolate ligand with all of the available lanthanide ions. We wanted to explore more fully the potential of the various $4f^n$ systems as shift reagents for a variety of organic molecules and to see if we could determine and understand the specific characteristics which produce the best shift reagents. More recent reports have established that (1) $Eu(dpm)_3$ itself (*i.e.*, without the pyridine molecules appended) is even better than the dipyridine adduct,[2] (2) the analogous praseodymium compound, $Pr(dpm)_3$, induces proton nmr shifts[3] of the opposite sign of those reported for $Eu(dpm)_3$ and also much larger than those reported for $Eu(dpm)_3$, (3) Eu(III), Gd(III), and Ho(III) cations will serve as nmr structural probes in several biological systems,[4] (4) when $Eu(dpm)_3$ serves as the shift reagent for adamantan-1- and -2-ol, the mechanism of deshielding involves interaction *both* through space (pseudocontact shift) and through bonds (contact shift),[5] and (5) $Eu(dpm)_3$ may be used as a shift reagent for a steroid and a triterpene.[6]

We have now prepared 47 compounds of the types $M(dpm)_3$ (M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), $M(dpm)_3py$ (M = same 12 metals), M-

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TABLE I

COMPOUNDS PREPARED IN THIS STUDY AND SOME CHARACTERIZING DATA

Compd	Color	Analysis						Mp,[a] °C	Magnetic moment[b]	Weiss constant
		C		H		N				
		Calcd	Found	Calcd	Found	Calcd	Found			
Ce(dpm)$_4$	Red	60.52	60.49	8.77	8.64	...	...	276	Diamag	
Pr(dpm)$_3$	Green	57.38	56.82	8.32	8.42	...	...	222–224	3.6, 3.7	
Pt(dpm)$_3$py	Green	59.29	59.74	8.12	8.22	1.82	1.75	...	...	
Pr(dpm)$_3$dipy	Green	60.98	60.28	7.74	7.77	3.31	3.14	191–193	3.6	
Pr(dpm)$_3$phen	Green	62.06	61.66	7.52	7.60	3.22	3.01	221–222	3.6	
Nd(dpm)$_3$	Violet	57.11	56.27	8.28	8.25	...	...	218–219	3.5, 3.7	
Nd(dpm)$_3$py	Violet	59.03	57.49	7.95	8.04	1.81	1.73	...	...	
Nd(dpm)$_3$dipy	Violet	60.74	59.25	7.70	7.67	3.29	3.14	189	3.7	
Nd(dpm)$_3$phen	Violet	61.82	61.44	7.49	7.59	3.20	3.18	222	3.7	
Sm(dpm)$_3$	White	56.61	56.47	8.21	8.46	...	...	200–201	2.1, 2.0	
Sm(dpm)$_3$py	White	58.57	58.02	8.02	8.14	1.80	1.64	133–135	2.4	
Sm(dpm)$_3$dipy	White	60.31	60.58	7.65	7.53	3.27	3.19	189–191	2.4	
Sm(dpm)$_3$phen	White	61.39	61.62	7.44	7.64	3.18	3.07	225–226	2.2	
Eu(dpm)$_3$	Yellow	56.48	56.58	8.19	8.41	...	...	190–191	3.6, 3.4	
Eu(dpm)$_3$py	White	58.45	58.66	8.00	8.17	1.79	1.76	135–138	3.7	
Eu(dpm)$_3$dipy	White	60.19	59.74	7.64	7.26	3.26	3.13	190–191	3.6	
Eu(dpm)$_3$phen	Light yellow	61.28	61.83	7.43	7.68	3.18	3.02	217–219	3.6	
Gd(dpm)$_3$	White	56.06	56.40	8.13	8.39	...	...	183–184	7.8, 7.6	175
Gd(dpm)$_3$py	White	58.06	56.85	7.95	7.95	1.78	1.65	134–135	7.8	
Gd(dpm)$_3$dipy	White	59.83	60.20	7.59	7.82	3.24	3.18	192–193	7.9	
Gd(dpm)$_3$phen	White	60.91	60.16	7.38	7.57	3.16	3.02	225–228	8.0	
Tb(dpm)$_3$	White	55.93	55.99	8.11	8.34	...	...	150–152	9.6	177
Tb(dpm)$_3$py	White	57.93	58.23	7.93	8.19	1.78	1.84	135–137	9.7	
Tb(dpm)$_3$dipy	White	59.71	59.81	7.58	7.61	3.24	3.27	195	9.7	
Tb(dpm)$_3$phen	Greenish white	60.80	61.27	7.37	7.56	3.15	3.22	241–242	9.7	
Dy(dpm)$_3$	White	55.65	55.96	8.07	8.40	...	...	182–183	10.3	173
Dy(dpm)$_3$py	White	57.67	57.95	7.77	8.10	1.77	1.98	135–137	10.7	
Dy(dpm)$_3$dipy	White	59.47	58.76	7.54	7.65	3.22	3.19	193	10.2	
Dy(dpm)$_3$phen	White	60.56	60.18	7.34	7.52	3.14	3.18	250	10.0	
Ho(dpm)$_3$	Yellowish white	55.46	55.67	8.04	8.25	...	...	178–180	10.0, 10.0	208
Ho(dpm)$_3$py	White	57.49	57.46	7.87	8.08	1.76	1.79	134–135	10.3	208
Ho(dpm)$_3$dipy	Light yellow	59.30	60.01	7.52	7.81	3.22	3.20	188–190	10.5	208
Ho(dpm)$_3$phen	Light yellow	60.39	61.07	7.32	7.58	3.13	3.13	246–248	10.3	208
Er(dpm)$_3$	Pink	55.28	54.89	8.01	8.20	...	...	179–180	9.3	187
Er(dpm)$_3$py	Pink	57.32	57.45	7.73	8.11	1.76	1.58	131–133	9.5	
Er(dpm)$_3$dipy	Pink	59.14	59.49	7.50	7.75	3.21	3.15	183	9.4	
Er(dpm)$_2$phen	Pink	60.24	60.79	7.30	7.53	3.12	2.97	254–256	9.5	
Tm(dpm)$_3$	White	55.15	55.30	7.99	8.24	...	...	170–173	7.2	152
Tm(dpm)$_2$py	White	57.21	57.27	7.83	8.00	1.76	1.65	134–136	...	
Tm(dpm)$_3$dipy	Light yellow	59.03	60.14	7.49	7.79	3.20	3.20	189–193		
Tm(dpm)$_3$phen	Light yellow	60.13	60.92	7.29	7.55	3.12	3.14	235–239	7.2	
Yb(dpm)$_3$	White	54.83	54.63	7.95	7.86	...	...	165–167	4.3, 4.3	173
Yb(dpm)$_3$py	White	56.91	56.85	7.79	7.97	1.75	1.62	130–132	4.5, 4.3	
Yb(dpm)$_3$dipy	White	58.75	58.69	7.45	7.69	3.19	3.22	167–168	4.3	
Yb(dpm)$_3$phen	White	59.85	60.63	7.26	7.62	3.10	3.11	...	4.3	
Lu(dpm)$_3$	White	54.69	54.35	7.93	8.00	...	...	173–174	Diamag	
Lu(dpm)$_3$py	White	56.78	55.54	7.77	7.74	1.74	1.62	125–127	Diamag	

[a] Dta and tga results generally support the melting point data and the former results may be obtained from the authors by those interested in the details. [b] Where there are two values listed, the first is the value obtained by the nmr technique and the second is the value obtained by the Gouy technique. Where there is only one value, the nmr technique was employed.

(dpm)$_3$dipy (M = same first 11 metals, but not Lu), M(dpm)$_3$phen (M = same first 11 metals, but not Lu), and Ce(dpm)$_4$. Elsewhere,[7] we shall deal with all of the various nmr studies involving these compounds and in particular their potential as proton shift reagents for various compounds. In this paper we describe the preparation and characterization of the lanthanide chelates and report the results of the nmr study of their magnetic moments and Weiss constants and of a low-temperature (77°K) study of their optical spectra.

Experimental Section

A. Preparation of Compounds. 1. The Tris(dipivaloylmethanato)metal(III) Compounds.—All 12 compounds (Pr–Lu, except Pm) were prepared by the method of Eisentraut and Sievers[8] and Berg and Acosta[9] with the difference that the compounds were purified by recrystallization three times from *n*-hexane rather than by sublimation. Results of elemental analyses are given in Table I along with other characterizing information. With cerium, the only product isolated had a 4:1 ligand-to-metal ratio and further experiments (*vide infra*) indicated that the product contains Ce(IV), leading to the simple formulation Ce(dpm)$_4$.

2. Pyridine Adducts of the Foregoing Compounds.—The 12 compounds (Pr–Lu, except Pm) were prepared by dissolving the tris(dipivaloylmethanate) in absolutely dry pyridine inside a drybox. The solution was left overnight in a tightly stoppered flask in the box. Then the excess pyridine was evaporated by evacuation in a vacuum desiccator. The dried product was dissolved in absolutely dry benzene and filtered, and the filtrate was evaporated to dryness in a vacuum desiccator. All operations were carried out in a dry, inert-atmosphere box. The compounds were stored in a desiccator over NaOH. Elemental analyses and other characterizing information are collected in Table I. The cerium compound, Ce(dpm)$_4$, did not yield a pyridine adduct.

3. 2,2′-Dipyridyl Adducts of the Tris(dipivaloylmethanates).—The 11 compounds (Pr–Yb, except Pm) were prepared by mixing in a 1:1 mole ratio the tris(dipivaloylmethanate) and the 2,2′-dipyridyl in the solvent carbon tetrachloride. Evaporation of the solvent yielded the desired 1:1 adduct, which was recrystallized three times from *n*-hexane. The cerium compound, as ex-

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(8) K. J. Eisentraut and R. E. Sievers, *ibid.*, **87**, 5254 (1965).

(9) E. W. Berg and J. J. C. Acosta, *Anal. Chim. Acta*, **40**, 104 (1968).

pected, did not yield an adduct compound. Elemental analyses and other characterizing data are collected in Table I.

4. 1,10-Phenanthroline Adducts of the Tris(dipivaloylmethanates).—These 11 compounds (Pr–Yb, except Pm) were prepared by exactly the same procedure used for the 2,2′-dipyridyl adducts, and again the cerium compound did not yield an adduct compound. Elemental analyses and other characterizing data are collected in Table I.

B. Physical Chemical Methods. 1. Thermal Properties.—Melting points were determined with a Thomas-Hoover Capillary Unimelt melting point apparatus. Differential thermal analysis (dta) curves were obtained with a Du Pont 900 instrument, using a heating rate of 20°/min in a nitrogen atmosphere. Thermogravimetric analysis (tga) was performed with a Du Pont 950 instrument, with the sample heated at the rate of 10°/min in a nitrogen atmosphere.

2. Spectral Properties.—A Cary 14 spectrophotometer was used for obtaining low-temperature optical spectra. Samples mulled in Nujol were smeared on filter paper which was then mounted on a brass plate which dipped inside an optical dewar flask containing liquid nitrogen.

3. Magnetic Properties.—Magnetic susceptibilities were measured using a Gouy balance in the case of compounds which had been prepared in sufficient quantity to permit these measurements. However, magnetic susceptibility was measured for all of the compounds at ambient temperature using Evans' nuclear magnetic resonance method.[10] The solvent used to prepare the standard solutions was a 1:1 mixture of CCl_4 and $CHCl_3$. The data were corrected for the diamagnetism of the ligands. Weiss constants, Δ, were determined for ten of the compounds in 1:1 CCl_4 and CH_2Cl_2 by measuring the magnetic susceptibilities by the nmr technique at several (usually six) temperatures between −90 and +38°. Employing the equation $\chi = C/(T + \Delta)$, the Δ values were taken from graphical plots of $1/\chi$ *vs.* T.

Results and Discussion

The compounds which were prepared for this study are listed in Table I, along with certain characterizing information. All of the "adduct" or mixed-ligand compounds, *i.e.*, those with pyridine, 2,2′-dipyridyl, or 1,10-phenanthroline, are new. However, it should be pointed out that several analogous mixed-ligand complexes have previously been reported, for example, 1:1 or 1:2 adducts of $Eu(dbm)_3$ (dbm = dibenzoylmethanide ion) with a number of oxygen- and nitrogen-containing Lewis bases,[11] $Ln(dpm)_3 \cdot DMF$ complexes,[12] and a few adduct products which contain one molecule of either dipy or phen attached to tris(β-keto enolate)-lanthanide ions.[13–15]

Our compounds, however, are the first to contain these latter bidentate nitrogen donors complexed to tris(dipivaloylmethanates). In view of the rather bulky nature of the β-keto enolate ligands, it is somewhat surprising to find that an additional bidentate ligand can still attach to the tris(dipivaloylmethanate) lanthanide ion, raising its coordination number to 8. Nevertheless, not only does the addition occur, but the thermal data (melting points, differential thermal analyses curves, and thermogravmetric curves) show that these compounds are roughly as stable as analogous adduct complexes[11] with less bulky β-keto enolates.

It is interesting to note that the procedure used to obtain $M(dpm)_3$ complexes for all other lanthanides yields a Ce(IV) compound, $Ce(dpm)_4$, with this element. Perhaps this result is due to a combination of factors which include (a) the greater ease of oxidation [Ce(III) → Ce(IV)] in the case of cerium and (b) the more favorable total bond energy associated with the utilization of four rather than three bidentate ligands.

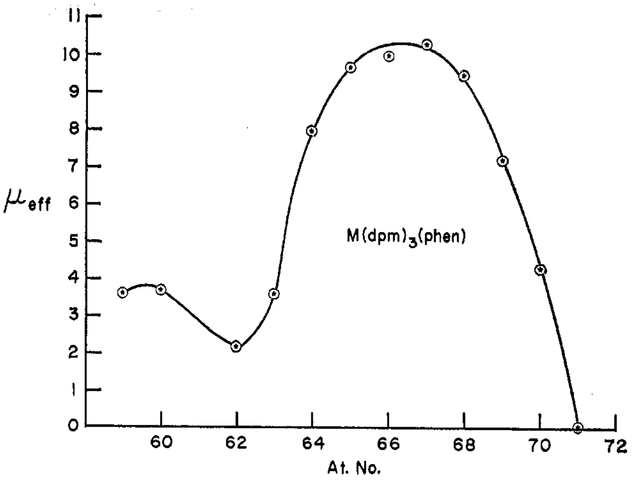

Figure 1.—Effective magnetic moments of the $M(dpm)_3$-phen complexes plotted *vs.* the atomic numbers of the metals, M.

TABLE II

OPTICAL SPECTRAL BANDS (CM^{-1}) OF PRASEODYMIUM COMPLEXES (GROUND STATE $^3H_4$)

$Pr(dpm)_3$	$Pr(dpm)_3dipy$	$Pr(dpm)_3phen$	$Pr(dpm)_3$ vapor[a]	Assignment[b]
		4,107 vw		
4,348 vvs		4,175 vvw		$^3H_6$
4,400 vs		4,405 m		
5,175 vvs		5,155 vw		
5,277 w		5,249 s	5,235	[$^3F_2$]
5,348 w		5,347 m		
5,806 s				
5,882 s				
5,917 s		5,952 vw		$^3F_3$
6,472 s				
6,579 s		6,579 s	6,578	
6,689 s		6,623 s		
6,969 s		6,981 m		
7,067 w		7,067 w		$^3F_4$
7,299 s		7,246 w		
8,403 m				$^1G_4$?
16,474 m	16,447 w	16,447 vw		
16,502 m				
16,543 m				
16,781 m	16,779 w	16,779 vw	16,835	
17,036 vvw				$^1D_2$
17,065 w	17,094 w	17,079 vw		
17,241 w		17,182 vw		
17,286 vw				
17,316 w			17,361	
			19,230 sh	
20,492 s		20,534 s	20,491 sh	$^3P_0$
20,534 s	20,555 s	20,619 vw		
20,929 m			20,920	
20,964 s				
21,110 m	21,075 m	21,097 s		$^3P_1$
21,142 w	21,119 vs			
21,231 w	21,322 m	21,322 s		
22,075 vs	22,272 m			
22,173 vm			22,123	$^3P_2$
22,421 w	22,523 s	22,523 m		

[a] Reference 13. [b] Assigned using collected data and assignments from G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals," H. M. Crosswhite and H. Crosswhite, Ed., Wiley, New York, N. Y., 1968. The brackets enclose the excited state of the "hypersensitive" transitions.

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TABLE III

OPTICAL SPECTRAL DATA FOR NEODYMIUM COMPLEXES (GROUND STATE $^4I_{9/2}$)

$Nd(dpm)_3$	$Nd(dpm)_3$ vapor[a]	$Nd(dpm)_3dipy$	Assignment[b]
	11,111		
11,494 vw	11,337	11,371 s	$^4H_{3/2}$
11,587 vw		11,501 m	
12,384 m	12,345	12,407 s	$^4F_{5/2}$
12,484 m	12,500	12,484 s	$^2H_{9/2}$
13,254 m			
13,319 m	13,297	13,351 m	$^4F_{7/2}$
13,432 m		13,441 m	
13,554 m	13,513	13,532 s	$^2S_{3/2}$
		15,873 vvw	$^2H_{11/2}$
	16,556 sh	16,708 m	
16,955 vs	16,883 sh	16,835 s	
17,050 vs	17,050	17,030 s	$\left\{\begin{matrix} ^4G_{5/2} \\ ^2G_{7/2} \end{matrix}\right\}$
17,079 vs		17,138 vvs	
17,153 w		17,206 vs	
17,212 w			
17,247 s		17,247 m	
17,301 s		17,307 vs	
17,331 vs	17,346		
17,452 vvs		17,422 vvs	
18,832 s	18,779		
18,875 m	18,867	18,939 s	
18,957 w		18,975 vs	$^4G_{7/2}$
19,011 m		19,011 vs	
19,238 w		19,158 m	
19,417 vw		19,399 s	
19,531 w		19,493 s	$^2G_{9/2}$
		19,743 vw	
19,960 vw		19,861 vw	
20,812 vw		20,756 vw	
		20,877 w	$^4G_{9/2}$
		21,075 w	
		21,420 vw	
		21,786 w	
23,202 vw	23,148	23,148 m	$^2P_{1/2}$
27,739 vw			$^4D_{3/2}$
27,972 vw			$^4D_{5/2}$
28,129 vw			
28,288 vw			$2I_{11/2}$
28,506 vw			$^4D_{1/2}$

[a] Reference 13. [b] See footnote *b* of Table II.

TABLE IV

OPTICAL SPECTRAL BANDS (CM^{-1}) OF SAMARIUM (GROUND STATE $^6H_{5/2}$) AND ERBIUM (GROUND STATE $^4I_{15/2}$) COMPLEXES

$Sm(dpm)_3$	$Sm(dpm)_3$ vapor[a]	Assignment[b]	$Er(dpm)_3$	$Er(dpm)_3$ vapor[a]	Assignment[b]
	6,289	[?][c]		6,578	$^4I_{13/2}$
	6,578		6,756 vw	6,756	
	6,993				
	7,462 sh			9,900	
				10,152	$^4I_{11/2}$
8,104	8,064			10,257	
8,183		$^6F_{7/2}$			
8,222 m				12,658	$^4I_{9/2}$
9,268 w	9,174		15,186 w		
9,330 w	9,293	$^4F_{9/2}$	15,244 vw	15,384	$^4F_{9/2}$
9,379 w	9,469		15,279 w	15,527	
17,737 vw		$^4G_{5/2}$	18,657 vw	18,518 sh	
			18,692 vw		$^4S_{3/2}$
18,939 w			18,727 vw	18,726	
18,961 w		$^4F_{3/2}$			
			18,957 s		
19,900 w			18,993 vvs		
20,052 w		$^4G_{7/2}$	19,048 s		[$^2H_{11/2}$]
			19,128 vs		
20,358 w			19,157 vs	19,157	
20,408 w	20,408	$^4I_{9/2}$			
			20,367 w		
20,929 vw		$^4M_{15/2}$, $^4I_{11/2}$	20,429 vw		
20,986 vw			20,492 vw	20,491	$^4F_{7/2}$
			20,525 vw		
21,400 vw	21,367 sh		20,576 vw		
21,645 vw		$^4I_{13/2}$			
			22,099 vw		$^4F_{5/2}$, $^4F_{3/2}$
22,198 vw		$^4F_{5/2}$, $^4G_{9/2}$	22,124 vw		
22,272 vw					
			24,510 vw		
23,742 vvs	22,935		24,570 vw		
23,895 m	23,809	$^6P_{5/2}$	24,600 vw	24,630	$^2H_{9/2}$
24,085 m				25,316 sh	
				25,773	
24,540 m					
24,649 vs		$^6P_{3/2}$, $^4I_{13/2}$	26,178 vvs	26,178	
24,759 vs			26,281 vs		$^4G_{11/2}$
			26,385 vs	26,385	
24,863 w					
24,900 w		$^4F_{9/2}$	27,285 m	26,809 sh	$^2G_{9/2}$
25,013 w				27,100 sh	
26,137 w			27,510 w	27,397 sh	$^2K_{15/2}$
26,385 w					
26,490 m			27,663 w		$^2G_{7/2}$
26,560 m		$^4K_{11/2}$			
26,666 m					
27,360 s					

[a] Reference 13. [b] See footnote *b* of Table II. [c] These bands fit no previous assignments.

We have much evidence that we are indeed dealing with Ce(IV) and not Ce(III), as *might* have formed if one of the four β-diketone molecules were still retaining its acidic proton. This evidence includes its diagmagnetism, its nmr spectrum which fails to show any unique acidic proton and which shows all β-keto enolate ligands to be equivalent, the failure of the compound to yield any adducts with py, dipy, or phen, the intense color and particular optical spectrum of the compound (no sharp bands, but rising absorption in the visible toward a charge-transfer peak in the ultraviolet), and its similarity in both color and melting point to the product reported earlier[6] and also formulated as $Ce(dpm)_4$. The melting points for the $M(dpm)_3$ compounds range from a high of 222° (for M = Pr) to a low of 165° (for M = Yb), whereas the $Ce(dpm)_4$ compound melts at 276°.

The new monopyridine compounds all melt at 134 ± 4°, except for the lutetium compound which melts at 125°. The new dipyridyl compounds melt at 189 ± 6°, except for the ytterbium compound which melts at 167°. The new 1,10-phenanthroline compounds from Pr to Gd melt at 221 ± 4° and from Tb to Yb melt higher at 245 ± 10°.

Although it is always risky speculating on the significance of melting points, it does appear clear that in the four series of complexes (plus $Ce(dpm)_4$) the melting points increase in the order $M(dpm)_3py$ < $M(dpm)_3dipy$ < $M(dpm)_3phen$ < $Ce(dpm)_4$. This order suggests that the seven-coordination species forms the least thermally stable lattice followed by the six-coordination species, which is less stable than the eight-coordination species. It is not clear to us, however, why the 1,10-phenanthroline compounds melt higher than the dipyridyl ones. Perhaps the rigidly planar phen ligand, which in its planarity is like the skeletal β-keto enolate anion, permits a more stable crystal packing. This suggestion is supported by the fact that the $Ce(dpm)_4$ compound has the highest melting point of all.

The magnetic moments, corrected for the diamagnetism of the ligands, are also listed in Table I. Most of the values are from nmr measurements and these compare well with the Gouy-determined values where the amount of sample permitted the latter determination to be made. If the values are plotted *vs.* increasing atomic number, the characteristic unequal double-humped curve (Figure 1) is obtained. The nmr technique for obtaining magnetic moments[10] thus has prov-

TABLE V

OPTICAL SPECTRAL BANDS (CM^{-1}) OF HOLMIUM (GROUND STATE $^5I_8$), DYSPROSIUM (GROUND STATE $^6H_{15/2}$), GADOLINIUM (GROUND STATE $^8S_{7/2}$), AND TERBIUM (GROUND STATE $^7F_6$) COMPLEXES

Ho(dpm)$_3$	Ho(dpm)$_3$ vapor	Assignment^b	Dy(dpm)$_3$	Dy(dpm)$_3$ vapor^a	Assignment^b
15,420 m	15,537			7,836	[$^6F_{11/2}$]
15,468 m					
15,564 m		$^5F_5$		7,936 sh	?
15,625 m					
15,686 m				9,090	$^6H_{7/2}$, $^6F_{9/2}$
	17,497				
18,446 vw	18,181 sh	$^5S_2$		10,695	$^6H_{5/2}$ or $^6F_{7/2}$
18,553 s	18,518			11,111	$^6F_{7/2}$
18,584 s		$^5F_4$			
18,612 s				12,345	$^6F_{5/2}$
18,681 s					
				17,605	?
20,437 vw					
20,488 m			21,017 vw		$^4F_{9/2}$
20,542 m	20,512	$^5F_3$	21,030 vw		
20,653 w			21,313 vw		
20,674 m			21,468 vw		
20,747 w					
			21,949 m		
20,942 vw			22,036 m	22,026	
21,151 w		$^5F_2$	22,065 m		
			22,134 m		$^4I_{15/2}$
21,186 w			22,198 m		
21,345 m			22,336 vw		
21,390 w			22,386 vw		
21,436 vw					
21,552 m		$^3K_8$	23,392 vw		$^4G_{11/2}$
21,575 vw			23,474 vw		$^4G_{11/2}$
21,687 m	21,645				
21,805 w			24,802 vw		
21,858 w			24,925 vw		
			25,013 vw		
21,915 s	21,905 sh		25,100 vw		
21,954 w			25,176 vw		
21,973 s	21,978 sh				
21,997 s			25,465 w		
22,085 s		[$^5G_6$]	25,562 m		
22,139 s			25,674 m		
22,193 vs					
22,267 s			25,940 vs		
22,316 vvs	22,321				
23,474 w			17,265 m		$^5D_0$
23,657 w	23,584 sh				
23,725 vw			18,779 m	18,656	
23,753 w	23,752	$^5G_5$	18,847 vw		$^5D_1$
23,866 m			18,986 vw		
23,895 m			19,029 vw		
23,952 m					
24,038 w			21,450 m		
			21,501 vs	21,482	[$^5D_2$]
25,820 vw	25,706		21,529 vs	21,598	
25,853 vw		$^5G_4$			
25,887 m			Gd(dpm)$_3$		Assignment
26,130 s	26,178	$^3K_7$	31,847 w		$^6P_{7/2}$
27,532 w			36,364 m		$^6I_{9/2}$, $^6I_{17/2}$,
27,412 w					
27,472 s			37,106 m		$^6I_{15/2}$, $^6I_{13/2}$
27,594 w		$^3H_5$, $^3G_2$			
27,693 s			40,816 m		$^6D_{5/2}$
27,755 s					
			Tb(dpm)$_3$		Assignment
			28,653 m		$^5D_2$, $^5G_4$, $^5L_8$
			31,008		

[a] Reference 13. [b] See footnote *b* of Table II.

en quite satisfactory with lanthanide complexes and so we extended its use to the evaluation of Weiss constants by carrying out the measurements for at least six temperatures between −90 and +38° for each of ten compounds. To our knowledge this is the first time such use has been made of the nmr technique. The compounds studied this way and their Weiss constants are listed in Table I. It was our intention to try to find some relationship between the magnetic properties of these complexes and their abilities as proton nmr (pseudocontact) shift reagents. This will be explored elsewhere[7] in the discussion of the nmr shift studies.

The 77°K optical spectral data for M(dpm)$_3$ (M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm), Pr(dpm)$_3$(*o*-phen), Pr(dpm)$_3$phen, and Nd(dpm)$_3$dipy are collected in Tables II–V. Included are the data obtained by Gruen, DeKock, and McBeth[16] on eight of the M(dpm)$_3$ compounds in the vapor phase. Assignments are made of most of the bands to transitions from the indicated ground level to the appropriate indicated SLJ level. The so-called "hypersensitive" transitions, *i.e.*, those whose intensities (in eight of the rare earths) are particularly and strongly dependent upon media, are bracketed in Tables II–V. Further interpretation of the optical spectral data is not warranted at this time, but a future paper will deal with the emission spectra of several of the complexes reported here.

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[16] D. M. Gruen, C. W. DeKock, and R. L. McBeth, *Advan. Chem. Ser.*, **No. 71**, 102 (1967).