

Anal. Calcd. for $C_{45}H_{33}EuO_6 \cdot H_2O$: C, 64.4; H, 4.2; Eu, 18.1. Found: C, 64.4; H, 4.4; Eu, 18.0.

18. Tris(1,3-diphenyl-1,3-propanediono)europium(III).—Tris(1,3-diphenyl-1,3-propanediono)europium(III) was dried

for 7 hr. under high vacuum at about 110° , m.p. $\sim 220^\circ$ dec.

Anal. Calcd. for $C_{45}H_{33}EuO_6$: C, 65.8; H, 4.1; Eu, 18.5. Found: C, 65.9; H, 4.2; Eu, 18.2.

[CONTRIBUTION FROM RCA LABORATORIES, PRINCETON, NEW JERSEY]

Octacoordinate Chelates of Lanthanides. Two Series of Compounds

BY HERBERT BAUER, JOSEPH BLANC, AND DANIEL L. ROSS

RECEIVED JULY 17, 1964¹

Two series of compounds of the compositions $C^+[(\beta\text{-diketonon})_4Ln(III)]^-$ and $(\beta\text{-diketonon})_3BLn(III)$ are reported in which C^+ is a substituted ammonium cation, B is a neutral bidentate ligand, and Ln is Eu, Gd, or Tb. Methods of preparation and physical properties, including fluorescence spectra, are presented. The chemical and spectroscopic evidence indicate that the eight oxygens in the tetrakis(β -diketonon) chelates are essentially equivalent and that the lanthanide ions in these compounds are octacoordinate.

Certain lanthanide ions possess sharp emission lines in the visible and infrared regions. The possibility of transferring energy efficiently to these ions by way of strongly absorbing transitions characteristic of organic ligands has motivated many workers to investigate lanthanide chelates as potential laser materials.²⁻⁴ The most widely studied of these chelates have been those having β -diketonones as the ligands and europium(III) as the central ion. For example, laser action has been observed in chelates of europium with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TFTBD) dissolved in a polymer matrix¹ and with 1-phenyl-1,3-butanedione (PBD) in alcoholic solutions.^{3,5,6} An inspection of the majority of the many publications describing studies of the spectroscopic properties of lanthanide β -diketonone chelates⁷⁻²¹ reveals little information regarding the methods of preparation of these materials. Melting points and analytical data are not presented, and in many cases no preparative details are given. A number of these papers refer to the work of Crosby, Whan, and Alire¹² who stated only that the chelates were precipitated from solutions of the lanthanide chloride and diketone in ethanol, water, or methanol by the addition of piperidine. In a later paper, Whan and Crosby²² reported a preparation of lanthanide tris(1,3-diphenyl-1,3-propanediono) (DPPD) chelates. In this proce-

cedure, an alcoholic solution of the lanthanide chloride and a 25% excess of DPPD was treated with piperidine and concentrated to precipitate the product. It was observed that it was necessary to submit the product to prolonged vacuum drying at $125\text{--}150^\circ$ to drive off an "extra mole of chelating agent." A number of workers^{5,15-18,20} have used this "piperidine method" to prepare chelates. More recently, other papers have confirmed that compounds made by this technique did not correspond to simple tris chelates. Indeed, the current literature gives evidence of considerable confusion regarding this matter. Metlay²³ studied both the initial product (designated by him EuD_4) obtained by the "piperidine method" and the compound obtained by drying (EuD_3) and showed them to behave differently. He suggested that " EuD_4 " was the tris chelate containing an additional weakly bonded mole of diketone. A similar explanation has been suggested²⁴ to explain similar behavior for the product obtained from europium and PBD by the "piperidine method" (EuB_4). Ohlmann and Charles²⁵ have also discussed EuD_3 and pointed out the possibility that " EuD_4 " might also contain piperidine. Winston and co-workers²⁶ condensed the material driven off from the analogous product from TFTBD and identified it as the piperidinium salt of TFTBD. Thus, it was recognized that the initial products from the "piperidine method" which uses an excess of diketone and piperidine contain an extra molecule both of piperidine and diketone. More recently, this has been observed by others.^{6,27}

Until recently, the trivalent lanthanide ions were thought to be hexacoordinate in their reactions with various chelating ligands, and a number of tris(β -diketonon)lanthanide(III) compounds have indeed been prepared and characterized.²⁸⁻³¹ It has been pointed out, however, that the nature of these products and, indeed,

- (1) A preliminary account was received May 16, 1964.
- (2) (a) N. E. Wolf and R. J. Pressley, *Appl. Phys. Letters*, **2**, 152 (1963); (b) E. H. Huffman, *Nature*, **200**, 158 (1963).
- (3) A. Lempicki and H. Samelson, *Phys. Letters*, **4**, 133 (1963).
- (4) E. J. Schimitscheck, *Appl. Phys. Letters*, **3**, 1107 (1963).
- (5) A. Lempicki and H. Samelson, Proceedings of the Symposium on Optical Masers, Polytechnical Press, Brooklyn, N. Y., 1963, p. 374.
- (6) A. Lempicki, H. Samelson, and C. Brecher, Fourth Annual Rare Earth Symposium, Phoenix, Ariz., April, 1964.
- (7) S. I. Weissman, *J. Chem. Phys.*, **10**, 214 (1942).
- (8) P. Yuster and S. I. Weissman, *ibid.*, **17**, 1182 (1949).
- (9) V. V. Kuznetsova and A. N. Sevchenko, *Bull. Acad. Sci. USSR Phys. Ser.*, **23**, 3 (1959).
- (10) G. A. Crosby and R. E. Whan, *J. Chem. Phys.*, **32**, 614 (1960).
- (11) G. A. Crosby and R. E. Whan, *Naturwiss.*, **47**, 276 (1960).
- (12) G. A. Crosby, R. E. Whan, and R. M. Alire, *J. Chem. Phys.*, **34**, 734 (1961).
- (13) G. A. Crosby and R. E. Whan, *ibid.*, **36**, 863 (1962).
- (14) N. Filipescu, M. R. Kagan, N. McAvoy, and F. A. Serafin, *Nature*, **196**, 467 (1962).
- (15) E. Nardi and S. Yatsiv, *J. Chem. Phys.*, **37**, 2333 (1962).
- (16) F. F. Rieke and R. Allison, *ibid.*, **37**, 3011 (1962).
- (17) M. L. Bhaumik, H. Lyons, and P. C. Fletcher, *ibid.*, **38**, 568 (1963).
- (18) H. Samelson and A. Lempicki, *ibid.*, **39**, 110 (1963).
- (19) E. J. Schimitscheck, *Appl. Phys. Letters*, **3**, 117 (1963).
- (20) N. McAvoy, N. Filipescu, M. R. Kagan, and F. A. Serafin, *J. Phys. Chem. Solids*, **25**, 461 (1964).
- (21) A. Lempicki and H. Samelson, *Appl. Phys. Letters*, **2**, 159 (1963).
- (22) R. E. Whan and G. A. Crosby, *J. Mol. Spectry.*, **8**, 315 (1962).

- (23) M. Metlay, *J. Chem. Phys.*, **39**, 491 (1963).
- (24) H. Samelson, A. Lempicki, V. A. Brophy, and C. Brecher, *ibid.*, **40**, 2547 (1964).
- (25) R. C. Ohlmann and R. G. Charles, *ibid.*, **40**, 3131 (1964).
- (26) H. Winston, O. J. Marsh, C. K. Suzuki, and C. L. Telk, *ibid.*, **39**, 267 (1963).
- (27) (a) M. L. Bhaumik, *et al.*, *J. Phys. Chem.*, **68**, 1490 (1964); (b) E. J. Schimitscheck and R. B. Nehrlich, Electrochemical Society Optical Maser Symposium, Recent News Papers No. 92c, Toronto, 1964.
- (28) J. G. Stites, C. N. McCarty, and L. L. Quill, *J. Am. Chem. Soc.*, **70**, 3142 (1948).
- (29) L. Sacconi and R. Ercoli, *Gazz. chim. ital.*, **79**, 731 (1949).
- (30) R. G. Charles and A. Perrotto, *J. Inorg. Nud. Chem.*, **26**, 373 (1964).
- (31) F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **40**, 2790 (1964).

TABLE I
LANTHANIDE TETRAKIS(β -DIKETONO) CHELATES
[substituted ammonium]⁺[(RCOHCOR')₄Ln(III)]⁻

R	R'	Cation	Ln	M.p. dec., °C.	Analyses, %									
					C		H		N		S		Ln	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Thienyl	CF ₃	2,4,6-Trimethylpyridinium	Eu	159-160 ^a	41.46	41.57	2.44	2.54	1.21	1.26	11.07	11.19	13.12	13.17
2-Thienyl	CF ₃	2,4,6-Trimethylpyridinium	Tb	155-157 ^b	41.20	40.87	2.42	2.56	1.20	1.17	11.00	11.26		
2-Thienyl	CF ₃	Isoquinolinium	Eu	170-171 ^b	42.20	41.88	2.07	2.35	1.20	1.04	10.99	10.70	13.02	12.97
2-Thienyl	CF ₃	(<i>n</i> -C ₈ H ₇) ₄ N	Eu	188-189 ^c	43.21	43.49	3.63	3.65	1.14	1.29	10.49	10.18	12.43	12.42
2-Thienyl	CF ₃	(<i>n</i> -C ₈ H ₁₃) ₄ N	Eu	170-172 ^c	48.34	48.22	4.93	4.92	1.01	1.22	9.22	8.95		
2-Thienyl	C ₆ H ₅	(<i>n</i> -C ₈ H ₇) ₄ N	Eu	189-193 ^d	61.23	60.92	5.14	5.10	1.12	0.99	10.22	10.38		
2-Thienyl	2-Thienyl	Piperidinium	Eu	180-186 ^e	49.90	49.95	3.42	3.54	1.19	1.27	21.75	22.02		
2-Thienyl	2-Thienyl	Piperidinium	Tb	182-188 ^f	49.60	49.80	3.40	3.75	1.18	1.25	21.62	21.63		
C ₆ H ₅	CF ₃	2,4,6-Trimethylpyridinium	Eu	168-170 ^b	50.80	51.01	3.20	3.29	1.23	1.40			13.39	13.32
C ₆ H ₅	CF ₃	Isoquinolinium	Eu	150-151 ^a	51.50	51.97	2.82	3.02	1.22	1.13			13.30	13.27
C ₆ H ₅	CH ₃	(<i>n</i> -C ₈ H ₇) ₄ N	Eu	158-166 ^a	63.53	63.29	6.56	6.49	1.42	1.42				
C ₆ H ₅	C ₆ H ₅	Piperidinium	α -Eu	184-187 ^f	69.02	68.79	4.99	4.89	1.24	1.19			13.44	13.54
			β	182-184 ^f		69.10		5.24		1.32				
C ₆ H ₅	C ₆ H ₅	Piperidinium	α -Gd	185-189 ^f	68.70	68.90	4.97	5.12	1.23	1.22				
			β	183-185 ^f		68.64		5.27		1.29				
C ₆ H ₅	C ₆ H ₅	(<i>n</i> -C ₈ H ₇) ₄ N	Eu	203-207 ^d	70.23	70.03	5.89	5.75	1.14	1.24			12.34	12.58
C ₆ H ₅	C ₆ H ₅	(<i>n</i> -C ₈ H ₁₃) ₄ N	Eu	220-226 ^d	72.08	71.71	6.91	6.61	1.00	1.14				
C ₆ H ₅	C ₆ H ₅	C ₈ H ₅ N(C ₂ H ₅) ₁₅ CH ₃	Eu	193-197 ^g	72.09	72.28	6.12	6.11	1.04	1.11				
C ₆ H ₅	C ₆ H ₅	Azabicyclononane ion	Eu	164-168 ^h	69.73	69.99	5.16	5.34	1.20	1.16				
C ₆ H ₅	C ₆ H ₅	(<i>n</i> -C ₈ H ₇) ₂ NH ₂	Eu	195-200 ^b	69.10	69.35	5.27	5.45	1.22	1.28				
β -C ₁₀ H ₇	CF ₃	Isoquinolinium	Eu	192-196 ^a	58.13	58.16	3.00	3.28	1.04	1.17				
CH ₃	CF ₃	Isoquinolinium	Eu	111-114 ^h	38.94	39.19	2.70	2.90	1.56	1.53				

Recrystallization solvents: ^a 2-Propanol. ^b Carbon tetrachloride. ^c Ethanol. ^d 2-Butanone. ^e Benzene. ^f Methanol. ^g Acetone-2-butanone. ^h Cyclohexane.

the reproducibility of the preparations were strongly dependent on the careful control of pH and order of mixing of the reagents.³² Often the tris chelates have been found to decompose on attempted recrystallization.³³ Recently published studies^{34,35} have demonstrated that some trivalent lanthanide ions in solution are capable of attaining coordination numbers higher than six, although this possibility has been suggested earlier.^{36,37} Even for simple β -diketone tris chelates, there have been indications that additional coordinate valences are available.^{30,31,38,39}

We have found that, in their reactions with β -diketones, Eu(III), Gd(III), and Tb(III) prefer to exhibit octacoordinate properties, and we wish to describe two series of chelates in which the lanthanide ion is so bonded to four bidentate ligands.

These are of the general types C⁺[β -diketono]₄lanthanide(III)⁻, where C⁺ is an ammonium cation, and [(β -diketono)₃B]lanthanide(III), where B is a neutral bidentate ligand such as 1,10-phenanthroline. We shall also discuss some aspects of the spectroscopic properties of these compounds both in the solid state and in solution.

Preparation and Chemical Characterization of Materials.—When a solution of a lanthanide(III) salt and 4 equiv. of diketone is neutralized with 4 equiv. of an appropriate amine (method A, see Experimental section), there are obtained, either as immediate or slow precipitates, or on evaporation of the solvent, compounds of the general formula: [substituted ammonium]⁺[(β -diketono)₄lanthanide(III)]⁻ in which

(32) Note, for example, the discrepancy in melting points given by ref. 29 and 30 for presumably identical Ln(DPPD)₃·H₂O chelates.

(33) Cf., for example, T. Moeller, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **14**, 69 (1953), and references cited therein.

(34) L. C. Thompson and J. A. Loraas, *Inorg. Chem.*, **2**, 89 (1963).

(35) L. C. Thompson and J. A. Loraas, *ibid.*, **2**, 594 (1963).

(36) L. Helmholz, *J. Am. Chem. Soc.*, **61**, 1544 (1939).

(37) L. W. Holm, G. R. Choppin, and D. Moy, *J. Inorg. Nucl. Chem.*, **19**, 251 (1961).

(38) J. R. Ferraro and T. V. Healy, *ibid.*, **24**, 1463 (1962).

(39) G. W. Pope, J. F. Steinbach, and W. F. Wagner, *ibid.*, **20**, 304 (1961).

the lanthanide ion appears to have a coordination number of eight. Compounds of this type have been prepared from a considerable number of β -diketones and a wide variety of organic amines.

Quaternary ammonium salts of this type may be prepared either by using 4 equiv. of a quaternary ammonium hydroxide (method B) or by neutralizing with 4 equiv. of sodium hydroxide a mixture of an equivalent of lanthanide salt, 4 equiv. of β -diketone, and 1 equiv. of a quaternary ammonium salt such as the chloride (method C). These compounds are well-characterized, highly crystalline solids and are readily purified by crystallization from organic solvents. Many of the europium compounds are brightly fluorescent even under incident diffuse daylight at room temperature.

It appears necessary to use an organic base sufficiently strong to ionize the particular diketone being used. Thus, no tetrakis chelate was obtained from DPPD when isoquinoline ($K_B = 2.5 \times 10^{-9}$) was employed, while the use of piperidine ($K_B = 1.6 \times 10^{-3}$) led to a well-defined product. On the other hand, TFTBD, a stronger acid than DPPD,⁴⁰ did form a tetrakis chelate with isoquinoline as the base. The melting points and analyses of a number of these compounds are listed in Table I.

We believe these materials to be examples of octacoordinated Ln(III), each lanthanide ion being surrounded by four equivalent β -diketone anions. The role of the organic base is to ionize the 4 moles of diketone and to serve (in the protonated or quaternary form) as the cation in these salts. The successful preparation of a number of quaternary ammonium salts (see Table I) suggests that it is unnecessary to postulate a coordination number higher than eight, since it is not possible for the quaternary ammonium ion to be a coordinating ligand. We propose that it is compounds of this general type that result from preparations using the "piperidine method" of Whan and Crosby²² and

(40) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953).

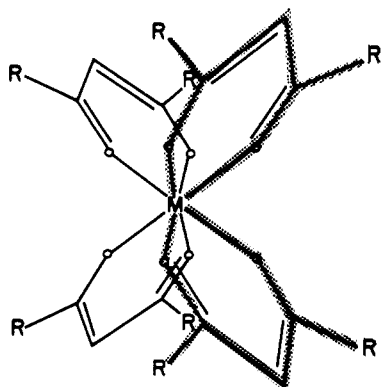


Fig. 1.—One of the possible isomeric structures of the $[(\text{RCO-CHCOR}')_4\text{Eu}]$ anion showing the four six-membered chelate rings and the attached R groups.

that have been studied by many of the workers referred to above. That these materials have spectroscopic properties significantly different from the tris chelates has been noted by Lempicki, Samelson, and Brecher,⁶ who observed that solutions of "EuB₄" exhibited laser action, while the material obtained by driving off the additional mole of diketone and piperidine was inactive. Some spectroscopic properties of these materials will be discussed below.

As can be seen from Fig. 1 and 2, a number of stereo- and geometric isomers is possible for the $[(\beta\text{-diketon})_4\text{-lanthanide(III)}]^+$ ion. In addition to the relatively large number of different isomers conceivable when an unsymmetrical β -diketone ($\text{RCOCH}_2\text{COR}'$), $\text{R} \neq \text{R}'$, is used, even symmetrical diketones (such as DPPD) permit a family of geometric isomers depending on the relative positions of the four ligands about the central ion. Undoubtedly, steric interactions among the R groups of the diketones will have an important effect on determining which configuration is the most favorable. Figure 1 shows that, with sufficiently large R groups, such interactions are quite likely. However, it also appears likely that the size of the ammonium cation and its spatial requirements in the crystal lattice will have an effect as well on the specific geometry of these compounds in the solid state. In several cases, we have actually isolated two different modifications of these compounds. A case in point is piperidinium tetrakis(1,3-diphenyl-1,3-propanediono)europium(III). The two forms have different melting points and show distinctly different emission spectra. Similar behavior was noted with the gadolinium analog of this compound (Table I) and with piperidinium tetrakis(1-phenyl-1,3-butanediono)europium(III).⁴¹ There is evidence that steric effects can even influence the success of the preparation of these tetrakis chelates. With dipivaloylmethane ($\text{R} = \text{R}' = t\text{-butyl}$), under the conditions of our preparative method, only the tris chelates analogous to those reported by Hammond⁴² were isolated. Presumably the bulky *t*-butyl groups prevent more than three ligands from approaching the lanthanide ion and shield it sufficiently to prevent even the formation of the usual hydrates.^{31,39}

A second general class of octacoordinate lanthanide β -diketone chelates that we report was prepared in an attempt to obtain neutral compounds that retain the

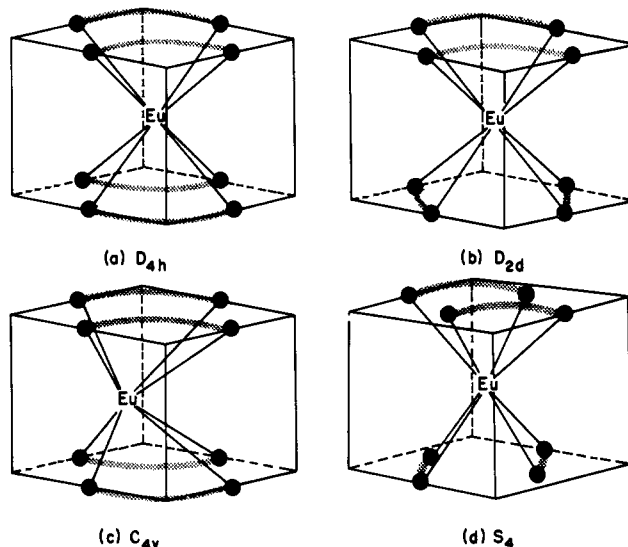


Fig. 2.—Four hypothetical structures of $[(\text{diketon})_4\text{Eu}]^-$ with different symmetries; the ligand bridges are indicated by the shaded bands and the oxygens by filled circles; the cubes are only for purposes of orientation; note that structure (c) can be obtained from (a) and (d) from (b) by small distortions.

octacoordinated structure of those discussed above but do not have their salt-like properties. Hart and Laming^{43,44} have shown that 1,10-phenanthroline is capable of coordinating to lanthanide ions. Inasmuch as 1,10-phenanthroline coordinates as a neutral bidentate ligand, it occurred to us that it should be possible to replace one molecule of diketone in the tetrakis chelate anion with one of 1,10-phenanthroline or a similar neutral bidentate ligand. When 1 equiv. of 1,10-phenanthroline is added to a solution containing 1 equiv. of lanthanide chloride and 3 equiv. of diketone, previously neutralized with 3 equiv. of sodium hydroxide (method D), materials of the general formula, tris(β -diketon)-(1,10-phenanthroline)lanthanide(III) are formed, often as immediate precipitates. 2,2'-Bipyridine has also been found to react in this manner. Several compounds of this type are listed in Table II.

Spectroscopic Data and Interpretation.—Detailed spectroscopic investigations of these chelates, such as quantum efficiency of fluorescence, polarized absorption and fluorescence from single crystals, and assignment of ligand field parameters will be reported elsewhere. Here, for the sake of simplicity, we would only like to report some fluorescence data which bear in a general way on the structure of various Eu chelates both in the crystalline state and in solutions.

The red fluorescence of Eu(III) in these chelates is usually due to transitions from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ levels of this ion. In the free, unperturbed ion, the lower state for fluorescence is fivefold degenerate; if the ion is placed in a nonspherical surrounding, some or all of this degeneracy will be removed. It should thus be possible to deduce some important aspects of the symmetry around the ion by observation of the number of fluorescent bands in this group of transitions. All the spectra of solid tetrakis chelates are consistent with eightfold coordination by oxygens. Table III shows the number of distinct, allowed electric dipole transitions for several different molecular symmetries of possible relevance with eightfold coordination by oxy-

(41) J. Blanc and D. Ross, unpublished results.

(42) G. S. Hammond, D. C. Nonhebel, and C. S. Wu, *Inorg. Chem.*, **2**, 73 (1963).

(43) F. A. Hart and F. P. Laming, *Proc. Chem. Soc.*, 107 (1963).

(44) F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, **26**, 579 (1964).

TABLE II
LANTHANIDE TRIS(β -DIKETONO)-1,10-PHENANTHROLINE CHELATES, [RCOCHCOR']₃(1,10-PHENANTHROLINE)LANTHANIDE(III)

R	R'	Ln	M.p., °C.	Analyses, %							
				C		H		N		S	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Thienyl	CF ₃	Eu	242-244 ^a	43.42	43.46	2.02	2.09	2.81	3.02	9.66	10.07
2-Thienyl	CF ₃	Tb	247-248 ^b	43.12	43.19	2.01	2.33	2.79	2.91	9.59	9.86
C ₆ H ₅	C ₆ H ₅	Eu	184-187 ^b	68.33	67.95	4.12	3.96	2.80	2.70		
C ₆ H ₅	CH ₃	Eu	192-194 ^c	61.84	61.92	4.32	4.66	3.43	3.64		
C ₆ H ₅	CF ₃	Eu	197-199 ^c	51.60	51.45	2.68	2.85	2.87	3.16		
(TFTBD) ₃ -2,2'-bipyridine		Eu	221-223 ^c	42.02	42.25	2.07	2.22	2.88	3.15		

Recrystallization solvents: ^a Acetonitrile. ^b Ethyl acetate. ^c 1:1 acetonitrile-methanol.

gens.⁴⁵ In order to give some measure of concreteness to these abstract symmetries, Fig. 2 illustrates four conceivable geometrical realizations of these compounds which give rise to symmetries D_{4h}, D_{2d}, C_{4v}, and S₄.⁴⁸ Ligand bridges have been indicated by arcs and oxygens by filled circles in Fig. 2. It should be realized that the structures shown are not the only ones compatible with the chemical evidence and the assumed symmetries. For instance, structures c and d show the Eu ion closer to one set of four oxygens than the other, which may well be the case for unsymmetrical chelating agents (R ≠ R'); the same symmetries, C_{4v} and S₄, although different structures, can be obtained with all oxygens equidistant from the lanthanide ion by tilting an appropriate set of four oxygens up and down from the top and bottom faces of the cube in structures a and b. The most symmetrical structure (D_{4h} in Fig. 2a) does not seem to occur since this group allows for no transitions, whereas all of our Eu chelates do fluoresce.

TABLE III
SUMMARY OF SELECTION RULES FOR THE ⁵D₀ → ⁷F₂ TRANSITIONS OF Eu(III) IN VARIOUS SYMMETRIES

Symmetry	Number of distinct allowed transitions
D _{4h}	0
D ₄	1
C _{4v}	2
C ₄	2
S ₄	3
D _{2d}	2
D ₂	3
C _{2v}	4
C ₂	5

A. Spectra of Solids.—The spectra shown in Fig. 3-6 are those obtained at 78°K., since, except for sharpening of bands, there are no differences in the spectra at 300 and 78°K. With one exception, discussed below, all of these europium tetrakis chelates show either two or three strong emission bands.

Inspection of Table III shows that, for two-band emission in the ⁵D₀ → ⁷F₂ transition, possible symmetries are C_{4v}, C₄, and D_{2d}. There is no possibility on spectroscopic grounds alone to choose among these three symmetries. It is important, however, that all three of these groups contain a fourfold axis of symmetry, which implies that the configuration of oxygens is very similar to those exhibited in Fig. 2.

(45) This summary of selection rules has been obtained from Tables IX and XIII of ref. 46 and Table X, Appendix X of ref. 47.

(46) J. L. Prather, "Atomic Energy Levels in Crystals," Monograph 19, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1961.

(47) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(48) The reader not familiar in detail with the significance of this group theoretical notation may want to consult Chapter 5 of ref. 47 for general background.

For those tetrakis chelates having three emission bands, Table III shows that either S₄ or D₂ are permissible symmetries. Here, however, a spectroscopic distinction is possible in principle since for S₄ symmetry two of the three allowed transitions have transition dipoles in the same direction with the third at a right angle to this direction⁴⁶; for D₂, on the other hand, the three allowed transitions are all at right angles to one another.⁴⁶ Thus, it should be possible to distinguish between D₂ and S₄ on the basis of experiments with polarized radiation on single crystals. In the one case we have so far examined (tetrahexylammonium (DPPD)₄Eu), the results⁴⁹ very strongly indicate S₄ symmetry.

The one exception to two- or three-band emission is the azabicyclononane salt of (DPPD)₄Eu, whose spectrum is shown in Fig. 3. It is seen that here there are five distinct emission bands. Of the groups listed in Table III, only C₂ predicts such a behavior, so that for this molecule there can be no fourfold axis of symmetry. A simple rationalization of the five emission bands observed is obtained by assuming that the top plane of oxygens, say in Fig. 2b, is rotated so as to place the top oxygens at corners of the cube rather than at midpoints of edges. Thus it seems to us that all of the general features demonstrated by these tetrakis chelates of Eu can reasonably be ascribed to structures that are very closely akin to one another.

This conclusion appears to be borne out by the two cases of isomerism we have so far detected. As indicated earlier, piperidinium (DPPD)₄Eu exists in two solid forms whose spectra are shown in Fig. 4. The less stable β -form shows a prominent doublet, whereas the α -form shows three emission bands with appreciable intensity. This may well represent an isomerism of the form D_{2d} ↔ S₄, since this requires only a slight distortion of the structure. It is particularly interesting that Brecher, *et al.*,⁵⁰ have found a similar spectroscopic behavior for the *same compound in solvents of different compositions*. In 75% ethanol-25% methanol at low temperatures, they find three strong emission bands; addition of small amounts of dimethylformamide to the solvent results in a two-band spectrum. Their results confirm the small energetic differences required to go from one fluorescent species to the other. The other case of isomerism is somewhat more difficult to understand. Spectra of α - and β -piperidinium (PBD)₄Eu are shown in Fig. 5. Here the two forms have qualitatively identical spectra with only two sharp bands (of about 2 Å. half-width). However, the α -form emits at 6123 and 6130 Å., while the β -form fluoresces at 6113 and 6135 Å. so that the splitting is quite

(49) J. Blanc, *J. Chem. Phys.*, to be published.

(50) C. Brecher, A. Lempicki, and H. Samelson, *ibid.*, **41**, 279 (1964).

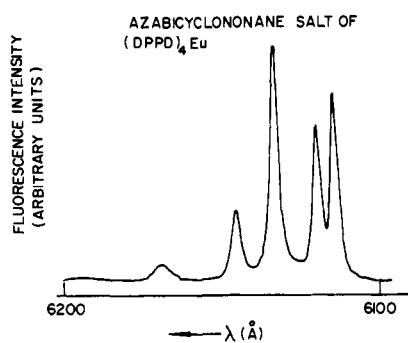


Fig. 3.—Fluorescence at 78°K. of the solid azabicyclononane salt of $(\text{DPPD})_4\text{Eu}$; the five-band spectrum indicates a symmetry of C_2 or lower.

different in the two cases. These spectra indicate an isomerism of the form $D_{2d} \longleftrightarrow C_{4v}$ or C_4 , which presumably involves a rotation of one set of four oxygens with respect to the other (see Fig. 2). It is possible, however, that one of the transitions allowed under S_4 is so weak that we have not detected it, in which case a D_{2d} - S_4 isomerism is possible.

Since isomeric forms of the same compound do not give rise to the same fluorescence spectra, it is perhaps not surprising that compounds with the same tetrakis chelate anion but with different cations also give rise to somewhat different spectra in the solid state. This is amply demonstrated in Table IV, which lists the spectra of three pairs of such compounds. In view of the relative ease with which different structures are assumed by these compounds, it may well be, as suggested earlier, that these spectroscopic differences are a sensitive probe to steric interactions between anion and cation. It should be remarked that the fluorescence efficiencies differ not only among compounds with the same anion and different cation but also in different isomeric forms of the same compound.⁵¹

TABLE IV
FLUORESCENCE OF EU TETRAKIS CHELATES AT 78°K.

Diketone	Cation	Wave length, Å.	In-tensity ^a	Half-width, Å.
DPPD	$(\text{C}_7\text{H}_7)_4\text{N}^+$	6111	100	9 ^b
		6113	100	
		6146	35	
DPPD	Piperidinium	6120	80	7 ^b
		6124	60	
		6130	100	
TFTBD	$(\text{C}_3\text{H}_7)_4\text{N}^+$	6117	100	6
		6134	35	14
		6168	25	14
TFTBD	2,4,6-Trimethylpyridinium	6106	100	2.5
		6142	20	4
		6158	10	5
TFPBD ^c	Isoquinolinium	6109	100	2.5
		6122	45	7
		6156	5	10
TFPBD ^c	2,4,6-Trimethylpyridinium	6119	100	2.5
		6142	25	7
		6165	6	10

^a Intensities are normalized to the most intense emission for each compound. ^b Peaks not fully resolved; half-width given is total of both peaks. ^c TFPBD = 4,4,4-trifluoro-1-phenyl-1,3-butanedione.

If one of the diketones in a lanthanide tetrakis chelate is replaced by a molecule of 1,10-phenanthroline,

(51) J. Blanc and D. L. Ross, work in progress.

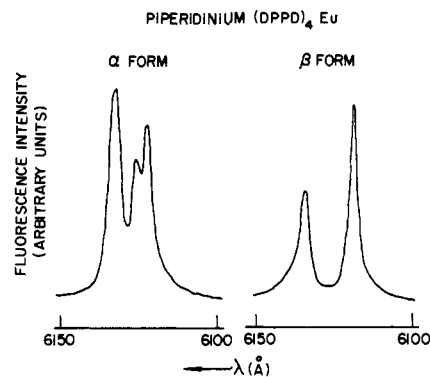


Fig. 4.—Fluorescence at 78°K. of the two solid forms of piperidinium $(\text{DPPD})_4\text{Eu}$; these spectra indicate an isomerism between forms of D_{2d} and S_4 symmetries.

the symmetry is appreciably lowered. If this replacement is made in a structure such as in Fig. 2b, the resulting symmetry is C_s ,⁴⁶ which allows for five emission bands. This is apparently what occurs with $(\text{TFTBD})_3$ - $(1,10\text{-phenanthroline})\text{europium}$ as shown in Fig. 6a. On the other hand, if the structure is derived from 2a, the molecule has C_{2v} symmetry allowing four transitions, and we have observed this behavior for $\text{tris}(4,4,4\text{-trifluoro-1-phenyl-1,3-butanedione})(1,10\text{-phenanthroline})\text{europium}$. In a qualitative way, what occurs here is that the long wave length transitions forbidden in the tetrakis chelate appear in the phenanthroline complex, but that the transitions at short wave lengths ($\approx 6110\text{-}6140$ Å.) are not perturbed to first order by the decrease in symmetry. Similarly, the compound $(\text{PBD})_2\text{EuOH}$, which is probably a polymeric chelate with oxol bridges, shows four emission bands (Fig. 6b) consistent with a C_{2v} symmetry. The "normal" tris chelates pose a more difficult problem. Figure 6c shows a spectrum of $(\text{TFTBD})_3\text{Eu}$ ⁵²; there are at least seven well-defined bands, whereas the maximum degeneracy of Eu(III) in the 7F_2 state is five. This means either that for the tris chelate some components of the emission arise from the ${}^5D_1 \rightarrow {}^7F_4$ transition which falls in the same energy range,⁵³ or that they all occur from 5D_0 , but some go to vibrationally excited states of the whole molecule.⁵⁴

B. Spectra of Solutions.—Tetrakis chelates in solution may be expected not only to show the isomerism already discussed for the solids, but also to be subject to a variety of dissociation reactions in which the lanthanide ion assumes a variety of coordinations with the diketones and the solvent molecules. These effects should be influenced by concentration and temperature as well as solvent composition and the particular diketones and cations used.

We have performed preliminary experiments in ethanol, toluene, and carbon tetrachloride. Table V is a summary of results obtained at room temperature with 10^{-4} M piperidinium $(\text{PBD})_4\text{Eu}$ in each of these solvents as well as with excess additions of 10^{-3} M piperidine or phenylbutanedione.⁵⁵ The solutions in the two nonpolar solvents are much more fluorescent than those in alcohol and show more detailed structure;

(52) Purchased from Distillation Products Industries.

(53) L. G. DeShazer and G. H. Dieke, *J. Chem. Phys.*, **38**, 2190 (1963).

(54) H. Samelson (private communication) has reported evidence that in similar systems all emission occurs from the 5D_0 state.

(55) α - and β -piperidinium $(\text{PBD})_4\text{Eu}$ yield identical solutions as judged by fluorescence and ultraviolet and visible absorption in alcoholic solutions and infrared absorption in carbon tetrachloride solution.

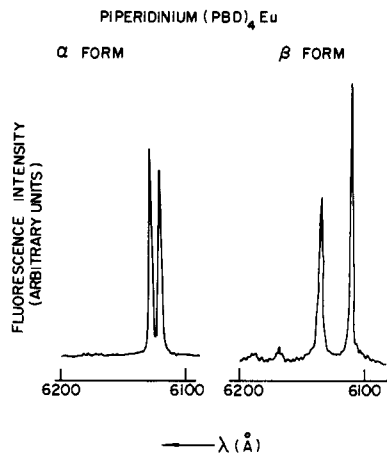


Fig. 5.—Fluorescence at 78°K. of the two forms of solid piperidinium (PBD)₄Eu; these spectra probably show an isomerism between forms of D_{2d} and C_{4v} symmetries.

in both carbon tetrachloride and toluene, it is possible to shift the fluorescence spectrum by addition of excess reagent so that it begins to resemble that of solid β -piperidinium (PBD)₄Eu although it is still superimposed on a broad emission background with little detail.

TABLE V
FLUORESCENCE OF 10⁻⁴ M PIPERIDINIUM (PBD)₄Eu IN DIFFERENT SOLVENTS^a

No excess	Excess piperidine	Excess PBD
	Ethanol	
6115 (100)	6115 (100)	6115 (100)
	Toluene	
6118 (100)	6111 (80)	6112 (100)
6135 (90)	6132 (100)	6127 (80)
6163 (40)		
	Carbon tetrachloride	
6093 (30)	6111 (70)	6112 (100)
6123 (100)	6131 (100)	6123 (74)
6163 (40)		6133 (65)

^a For each of the solutions, peaks of fluorescence intensity are indicated in Å., with intensity (normalized to the most intense in each solution) indicated in parentheses.

These solvents do not always glass smoothly upon cooling, nor is there any assurance that precipitation is not occurring. Nonetheless, the fluorescence spectra obtained at 78°K. present a consistent picture. At a concentration of 10⁻⁴ M piperidinium (PBD)₄Eu in ethanol, the fluorescence spectra at 78°K. showed three relatively sharp bands at 6115, 6135, and 6160 Å. with intensity ratios of 2:2:1 whether or not piperidine or phenylbutanedione was added in excess. However, if the concentration was raised to 10⁻³ M, the resulting spectra showed bands at 6113 and 6138 Å., with the second band about 2/3 as intense as the first. This spectrum is remarkably close to that of solid β -piperidinium (PBD)₄Eu, but the solution emits at somewhat longer wave lengths and the half-width of the emission is three to four times as large as that of the solid. In the mixed alcohol solvent used by Samelson, *et al.*,^{24,50}

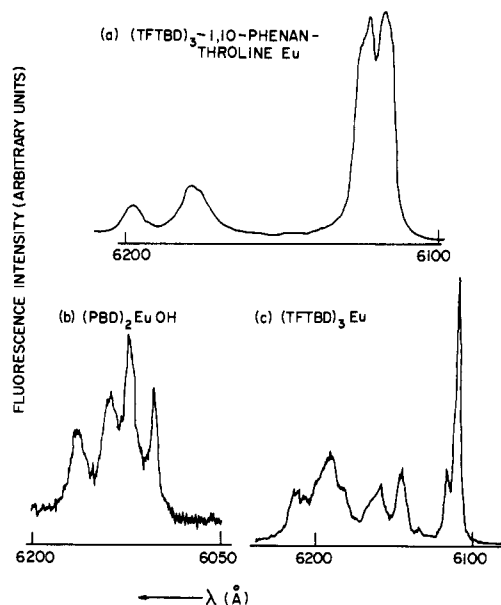


Fig. 6.—Fluorescence at 78°K. of three crystalline chelates: (a) (TFTBD)₃(1,10-phenanthroline)europium (the spectrum is consistent with a structure of C_s symmetry); (b) (PBD)₂EuOH (the spectrum indicates a C_{2v} symmetry for this compound); (c) (TFTBD)₃Eu (the large number of emission bands in the spectrum poses a spectroscopic problem).

the emission apparently shifts to still longer wave lengths. In toluene and carbon tetrachloride, the low temperature spectra were essentially identical with those at room temperature, except that, in some cases, some rather broad bands emerged from the background at wave lengths of \approx 6175 and 6200 Å.

We have also performed similar experiments on tetrakis(TFTBD) chelates. In all cases we have so far studied, the solution spectra appear very similar to each other, and to solution and solid spectra of (TFTBD)₃-Eu. On the other hand, solution spectra of the (diketonato)₃(1,10-phenanthroline)europium chelates appear to be identical, except for broadening, with those of the corresponding solids.

Discussion

There is little doubt both from the synthetic and spectroscopic data that we have synthesized lanthanide chelates which are in eightfold coordination, at least in their solid forms. The preparation of tetrakis chelate anions with tetraalkylammonium cations shows that it is not necessary to invoke ninefold coordination, while the successful substitution of a diketonate anion with a neutral bidentate ligand indicates that it should be possible to prepare octacoordinate complexes of lanthanide(III) ions with agents other than diketones. The spectroscopic data we have presented for the solid Eu tetrakis chelates strongly support the contention that all eight oxygens are essentially equivalent in the molecular structure. It would appear, however, that it is difficult to retain the structural integrity of the tetrakis chelates in solution; for the simplest explanation we can give to our solution data suggests that, except at low temperatures and high concentrations, equilibria in solution lead to mixtures of fluorescent species. Thermodynamic studies of such solutions would probably be of great help in unraveling the complexities of solution spectra.

We do not know what bonding types are involved in

these compounds, but the variety of structures suggested by the fluorescence spectra of tetrakis chelates in different solid environments probably cannot be accounted for in terms of a conventional directed valence theory. It may not be amiss here to speculate that some admixture of π -orbital bonding from the quasi-aromatic chelate rings to the lanthanide ion may be of significance in the stability and structure of these compounds.

In this article, we have barely touched on questions of quantum efficiency of fluorescence, ligand-field parameters, and comparisons between Eu, Tb, and Gd. In future publications, we hope to explore these and related questions, for it seems to us that the study of fluorescence from lanthanide chelates of known composition and structure can provide us with a sensitive tool for exploring luminescence problems in general.

Experimental⁵⁶

Chelating Agents.—1,3-Diphenyl-1,3-propanedione, 1-phenyl-1,3-butanedione, 2,4-pentanedione, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, 2,2'-bipyridine, and 1,10-phenanthroline were purchased from Distillation Products Industries. 4,4,4-Trifluoro-1-phenyl-1,3-butanedione, 1,1,1-trifluoro-2,4-pentanedione, and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione were purchased from Penninsular Chemical Research, Inc., Gainesville, Fla. 1-Phenyl-3-(2-thienyl)-1,3-propanedione,⁵⁷ 1,3-di(2-thienyl)-1,3-propanedione,⁵⁷ and 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione⁵⁸ were synthesized according to procedures described in the literature.

Piperidinium Tetrakis(1,3-diphenyl-1,3-propanedione)europium (III). **Method A.**—To a solution of 8 mmoles of 1,3-diphenyl-1,3-propanedione and 2 mmoles of europium chloride⁵⁹ in 70 ml. of hot ethanol was added 8 mmoles of piperidine. The solution was allowed to stand and cool to room temperature. The well-formed yellow needles which separated were collected, washed with water, dried under vacuum, and weighed 2.07 g. (91.5%). When 0.50 g. of the product was recrystallized from 25 ml. of absolute methanol, there first appeared the " β -form" as light yellow, feathery needles, m.p. 182–184°. Within 1 hr., these slowly began to redissolve in the methanol and the " α -form," dense, yellow blocks, m.p. 184–187°, slowly deposited over a 24-hr. period. Both forms gave correct elemental analyses (Table I).

Tetrapropylammonium Tetrakis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione]europium(III). **Method B.**—To a solution of 8 mmoles of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione and 2

mmoles of europium chloride in 75 ml. of hot ethanol was added 8 mmoles of 10% aqueous tetrapropylammonium hydroxide. On cooling the solution deposited 1.32 g. of brightly fluorescent, coarse, light orange crystals. On dilution of the filtered mother liquors with 75 ml. of water, an additional 0.54 g. of product was obtained (total yield 76%). An analytical sample was obtained by recrystallization from ethanol.

N-Hexadecylpyridinium Tetrakis(1,3-diphenyl-1,3-propanedione)europium(III). **Method C.**—To a solution of 8 mmoles of 1,3-diphenyl-1,3-propanedione, 2 mmoles of europium chloride, and 2 mmoles of N-hexadecylpyridinium chloride in 70 ml. of hot ethanol was added 4.0 ml. of 2.0 N sodium hydroxide solution with stirring. A dense off-white microcrystalline precipitate separated immediately. After the mixture had cooled, the solid was collected and recrystallized from 1:1 acetone–2-butanone to give 2.00 g. of product (74%).

Tris(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione)-1,10-phenanthrolineeuropium(III). **Method D.**—To a hot solution of 6 mmoles of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione and 2 mmoles of terbium chloride in 50 ml. of ethanol and 5 ml. of water was added 3.0 ml. of 2.0 N sodium hydroxide solution. The solution was filtered while hot from precipitated sodium chloride, and to it was added 2 mmoles of 1,10-phenanthroline monohydrate in 10 ml. of ethanol. Within 15 sec., a granular precipitate formed. The cooled reaction mixture was filtered and the collected precipitate, after washing with water and drying under vacuum, weighed 1.60 g. (80.5%). An analytical sample was recrystallized from ethyl acetate.

Solvents.—Solvents used for fluorescence studies were: absolute ethanol, Gold Shield alcohol, Commercial Solvents Corp.; toluene, analytical reagent, Mallinckrodt; and carbon tetrachloride, spectroquality, Matheson Coleman and Bell. These were used without further purification.

Spectra.—Fluorescence spectra were obtained with the aid of an 0.5-m. Jarrel-Ash monochromator. Excitation was obtained by conventional mercury or neon sources with appropriate filters. Detection was with an RCA 7265 photomultiplier with S-20 response. The spectra reproduced here were obtained with 1-Å. spectral resolution at convenient scanning speeds. Infrared absorption spectra either of KBr disks or CCl₄ solutions were measured on a Perkin-Elmer Model 221 spectrophotometer. Absorption in the visible and ultraviolet was measured either on a Cary Model 14 spectrophotometer for high resolution work or on a Perkin-Elmer Model 202 for surveys.

Acknowledgments.—We are grateful for the able assistance of S. M. Bennet and E. V. Fitzke in carrying out this work. We have benefited from discussions with many of our colleagues, particularly E. F. Hockings, H. A. Weakliem, J. Goldmacher, and N. E. Wolff. We wish to thank K. L. Cheng for the lanthanide analyses. After initial submission of our manuscript, we learned that L. R. Melby and N. J. Rose of the Central Research Department, E. I. du Pont de Nemours and Co., had independently performed research closely analogous to that reported here. We are grateful to Drs. Melby and Rose for a preprint of their work.

(56) Melting points are uncorrected and were determined on a Mel-Temp capillary melting point apparatus. Organic microanalyses were by Dr. S. M. Nagy, Massachusetts Institute of Technology.

(57) S. R. Harris and R. Levine, *J. Am. Chem. Soc.*, **70**, 3360 (1948); J. K. Sneed and R. Levine, *ibid.*, **72**, 5219 (1950).

(58) J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950).

(59) American Potash and Chemical Corp.