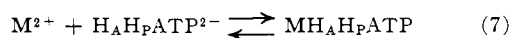


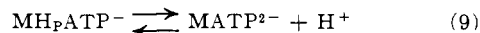
variously on determination of the activity of uncomplexed metal ion (colorimetric), activity of uncomplexed ATP (resin adsorption), or activity of displaced protons (titrimetric).<sup>23</sup> From the infrared results it appears that the agreement between titrimetric and the other methods is fortuitous. If the displacement of proton from the triphosphate group alone is measured, as in the present work, a low value for  $\log K_f$  results. The assumption that a prior complex formation occurs at the adenine moiety, with consequent increase in the acidity of the proton bound to  $N_1$ , serves to remove the discrepancy. There is good reason for believing, however, that the increased acidity of that proton does not result from complex formation there, but is merely a manifestation of complex formation at the triphosphate group, *without loss of terminal proton*. Watanabe, Evenson, and Gulz<sup>12</sup> have shown that  $Ca^{2+}$  and  $Mg^{2+}$  both cause a marked reduction of fluorescence in ATP at pH values as low as 2. The reduction in fluorescence is ascribed to interference on the part of the metal ions with triphosphate-adenine interaction,<sup>24</sup> as a result of metal ion coordination. Furthermore, Cohn and Hughes<sup>11</sup> have cited n.m.r. evidence for coordination of  $Mn^{2+}$  with  $H_PATP^{3-}$ . An increase in the acidity of the adenine proton might very well result as an additional consequence of the metal ion coordination; there is n.m.r. evidence for it in the case of  $Mg^{2+}$  coordination. It is obvious that if coordination of metal ion occurs at the triphosphate group in acid medium without an equivalent displacement of proton, the titrimetric method cannot be employed for accurate evaluation of formation constants.

The influence of the metal ion on the acidity of the adenine proton is increasingly evident as the over-all strength of metal ion binding to the triphosphate group increases (Table I). This may be ascribed to increasingly larger formation constants for binding of metal ions to the triphosphate group in advance of ionization of the terminal proton. In summary, the equilibria proposed are



(23) There is a discrepancy in the agreement of Nannings's<sup>7</sup> values for  $K_f$ , obtained by the pH shift method, and the other values listed. The pH shift method does not involve displacement of proton from adenine, and should therefore yield a lower value for  $K_f$  than the other methods, including a general titrimetric procedure.<sup>8,9</sup>

(24) B. H. Levedahl and T. W. James, *Biochim. Biophys. Acta*, **21**, 298 (1956).



In the case of  $Ca^{2+}$  and  $Mg^{2+}$ , equilibrium 8 occurs at a lower pH than (9); for the other metal ions, the two processes occur in the same pH range or, as in the case of  $Cu^{2+}$ , become reversed in order. In any case, it is assumed that the deprotonation effect observed at the  $N_1$  position results from the first equilibrium. It must be said, however, that it is not possible to say, on the basis of information presently available, that the increased acidity at  $N_1$  is not due in some measure to an interaction between the coordinated metal ion and the adenine moiety. The metal ion may be weakly complexed to the 6-amino group or the  $N_7$  nitrogen, or the complex may persist in a folded configuration so that an appreciable field effect is experienced at  $N_1$ .<sup>25</sup> The proton resonance shifts and broadenings observed<sup>11</sup> for the zinc, copper, and manganese complexes could also arise from field effects as well as from specific coordination at  $N_7$ .

In view of the argument presented above, neither the pD shifts measured in the infrared nor pH titrimetric data<sup>8,26</sup> can be employed in calculating reliable values of the formation constants for the divalent metal ions. The most that can be said is that the changes in acidity of the triphosphate proton establish a lower bound for the formation constants and that the relative magnitudes of the shifts in pD values for half-reaction probably correspond to the relative order of formation constants. In this connection, it should be noted that  $Ni^{2+}$  and  $Zn^{2+}$  are inverted in order on the basis of the infrared data as compared with the titrimetric<sup>8</sup> results.

The infrared data do not permit any conclusions to be drawn as to whether ATP coordinates to the various metal ions as a bidentate or tridentate ligand. This question has been discussed in connection with <sup>31</sup>P n.m.r. studies.<sup>11</sup> Further, the absence of significant frequency shifts on coordination, other than those due to loss of proton, preclude any meaningful conclusions about the hydrolysis of the bound, aquated metal ion.<sup>13</sup> It is possible that the acidity of water molecules bound to the coordinated metal ion is enhanced, and that this might affect the apparent acidity of the proton bound to the terminal phosphate. The infrared results, however, show only that the proton attached to the triphosphate group is made more acidic by coordination; there is therefore no evidence for the "localized hydrolysis" proton transfer suggested by Brintzinger.<sup>13</sup>

(25) H. Handschin and H. Brintzinger, *Helv. Chim. Acta*, **45**, 1037 (1962).

[CONTRIBUTION NO. 980 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

## Synthesis and Fluorescence of Some Trivalent Lanthanide Complexes

By L. R. MELBY, N. J. ROSE, E. ABRAMSON, AND J. C. CARIS

RECEIVED JULY 17, 1964

A variety of new trivalent lanthanide complexes has been prepared. They include tris( $\beta$ -diketone) chelates complexed with bidentate ligands of the phenanthroline type, and with N- and P-oxide donors. Of particular interest is a broad class of anionic tetrakis( $\beta$ -diketone) derivatives which we believe to be eight-coordinate. Well-resolved fluorescence emission spectra of several europium complexes are recorded.

The coordination chemistry of the lanthanide elements has been largely characterized by complexes

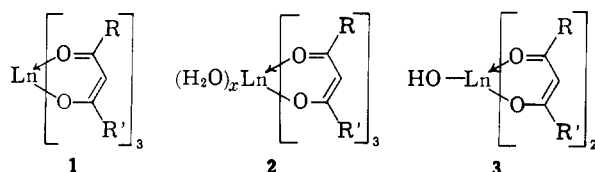
with oxygen-containing donors, particularly  $\beta$ -diketones. These derivatives have been formulated as

TABLE I  
 LANTHANIDE COMPLEXES WITH NEUTRAL DONORS

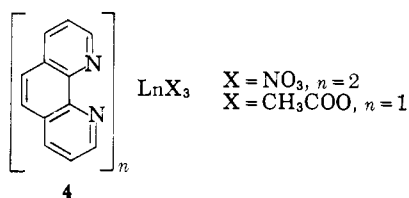
Complex <sup>a</sup>	Method	Yield, %	M.p. dec., °C.	% C		% H		% Ln		% Other	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
(PicNO) <sub>3</sub> EuCl <sub>3</sub>	1	68	190–192	37.0	37.1	3.6	4.0			N 7.2	6.9
(TPPO) <sub>3</sub> EuCl <sub>3</sub>	1	40	>280	59.3	59.1	4.2	4.4	13.9	14.8	Cl 18.2	18.3
(PicNO) <sub>3</sub> EuI <sub>3</sub>	1			41.0	41.1	4.0	4.2			P 8.5	8.5
(PicNO) <sub>3</sub> Eu(ClO <sub>4</sub> ) <sub>3</sub>	2	22.5	Explodes	43.6	43.4	4.3	4.9			Cl 9.7	9.5
(PicNO) <sub>3</sub> Eu(PF <sub>6</sub> ) <sub>3</sub>	3	27	185–190	39.5	39.0	3.9	3.8	10.4	11.1	N 8.0	8.1
(Phen)Eu(OAc) <sub>3</sub>	4	76	>280	42.5	42.1	3.4	3.6	29.9	29.4	I 27.0	28.0
(Phen) <sub>2</sub> EuCl <sub>3</sub> ·3H <sub>2</sub> O	4	74	>300	42.8	42.8	3.3	3.4	22.6	22.8	N 8.5	8.0
(Phen) <sub>2</sub> Eu(NO <sub>3</sub> ) <sub>3</sub>	4	78	>300	41.3	41.3	2.3	2.6	21.8	21.8	Cl 8.0	7.9
(Tripy)EuCl <sub>3</sub> ·H <sub>2</sub> O	4	86	>300	35.3	35.0	2.6	2.7			N 7.7	7.4
(Tripy)Tb(NO <sub>3</sub> ) <sub>3</sub> ·H <sub>2</sub> O	4	63	<300	30.2	30.6	2.3	2.2			F 23.4	23.4
										N 5.5	5.7
										Cl 15.8	16.1
										N 14.0	13.9
										Cl 20.9	20.4
										N 14.1	13.0

<sup>a</sup> Abbreviations: PicNO, 4-picoline N-oxide; TPPO, triphenylphosphine oxide; Phen, 1,10-phenanthroline; Tripy, tripyridyl.

simple tris-(β-diketonates)<sup>1</sup> (1), their hydrates<sup>2</sup> (2), or as the hydroxo bis(β-diketonates) (3).



The latter are probably polymeric.<sup>2b</sup> Other examples with oxygen donors include the six-coordinate hexa-(antipyrine) derivatives<sup>3</sup> and addition compounds between tris(β-diketonate) chelates and triphenylphosphine oxide or pyridine N-oxide as well as similar oxygen-containing bases.<sup>4–6</sup> Lanthanide complexes containing nitrogen donor groups are exemplified by the polyaminopolycarboxylate derivatives<sup>7</sup> and 8-hydroxyquinoline derivatives.<sup>8</sup> More recently, europium(III) tris(β-diketonates) complexed with monocyclic nitrogen donors such as pyridine or piperidine have been described.<sup>9</sup> In addition, several new 1,10-phenanthroline chelates of type 4 have been reported.<sup>10</sup> The constitu-



tion of many of these examples indicates the variability of coordination number for the lanthanides for which the higher coordination numbers seven and eight have been suggested<sup>11</sup> and nine-coordination demonstrated.<sup>12</sup>

(1) (a) W. Biltz, *Ann.*, **331**, 334 (1904); (b) R. E. Whan and G. A. Crosby, *J. Mol. Spectry.*, **8**, 315 (1962); (c) F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **40**, 2790 (1964).

(2) (a) G. Jantich and E. Meyer, *Ber.*, **53**, 1577 (1920); (b) G. W. Pope, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **20**, 304 (1961); (c) L. Sacconi and R. Ercoli, *Gazz. chim. ital.*, **79**, 731 (1949).

(3) Once thought to coordinate through nitrogen, the antipyrine molecule is now believed to bond through its oxygen atom: see L. G. Van Uiter and R. R. Soden in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 613.

(4) J. R. Ferraro and T. V. Healy, *J. Inorg. Nucl. Chem.*, **24**, 1463 (1962).

(5) R. G. Charles and A. Perrotto, *ibid.*, **26**, 373 (1964).

(6) F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **41**, 157 (1964).

(7) T. Moeller and E. P. Horwitz, *J. Inorg. Nucl. Chem.*, **12**, 49 (1959).

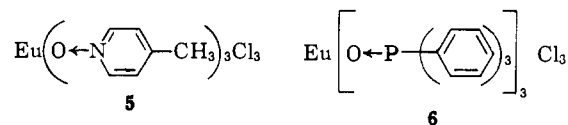
(8) T. Moeller and D. E. Jackson, *Anal. Chem.*, **22**, 1393 (1950).

(9) R. C. Ohlmann and R. G. Charles, *J. Chem. Phys.*, **40**, 3131 (1964).

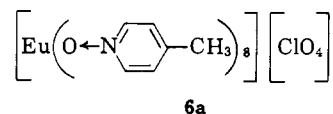
(10) F. A. Hact and F. P. Laming, *Proc. Chem. Soc.*, 107 (1963); *J. Inorg. Nucl. Chem.*, **26**, 579 (1964).

Our studies have sought to broaden some of these areas of rare earth coordination chemistry, and accordingly we have prepared a variety of new crystalline complexes and systematized a number of preparations. Of particular interest is a broad class of compounds, the anionic tetrakis(β-diketonate) derivatives, which we believe are eight-coordinate. We have included some qualitative comments on fluorescence intensity of some of the europium and terbium compounds<sup>13</sup> and have included a section in which well-resolved fluorescence emission spectra of several europium complexes are recorded.<sup>14</sup>

**Complexes with Neutral Donors (Table I).**—4-Picoline N-oxide<sup>15</sup> and triphenylphosphine oxide interact with europium(III) chloride to form crystalline compounds corresponding to compositions formulated as 5 and 6. On the other hand, the less nucleophilic



perchlorate ion permits the binding of eight molecules of the N-oxide donor, allowing isolation of a compound corresponding to 6a. From the N-heterocyclic donors,



1,10-phenanthroline or tripyridyl, and the appropriate lanthanide salt, we obtained crystalline derivatives corresponding to 7, 8, and 9 which are analogous to the previously reported compounds of type 4.<sup>16</sup> The infrared spectra of these three compounds show strong absorption at 3 μ attributed to the water of hydration.

(11) (a) J. L. Hoard, G. S. Smith, and M. Lind, "Advances in the Chemistry of Coordination Compounds," ref. 3, p. 302; (b) L. W. Holm, G. R. Choppin, and D. Moy, *J. Inorg. Nucl. Chem.*, **19**, 251 (1961).

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

(13) Fluorescence was visually monitored under irradiation with a 3660-Å. Mineralight lamp.

(14) In a private communication with Dr. Daniel L. Ross of the RCA Laboratories, Princeton, N. J., we learned of their independent work on the tetrakis(β-diketonates): H. Bauer, J. Blanc, and D. L. Ross, *J. Am. Chem. Soc.*, **86**, 5125 (1964).

(15) For leading references to complexes of pyridine N-oxides with first transition series ions, see D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

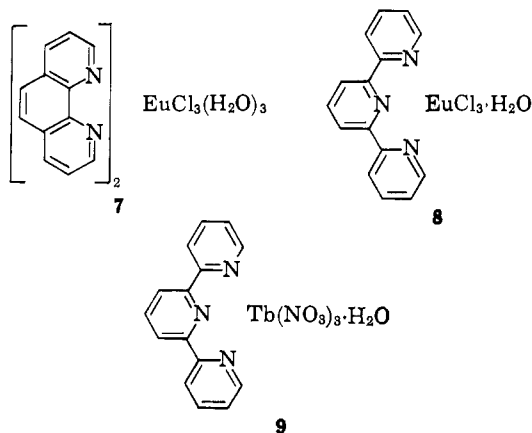
(16) Our work was completed prior to the publication of ref. 10. For completeness we have included analytical data in Table I.

TABLE II  
 β-DIKETONATES COMPLEXED WITH NITROGEN AND OXIDE DONORS

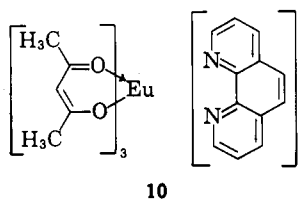
Complex <sup>a,b</sup>	Yield, %	M.p. dec., °C.	% C		% H		% Ln		% Other				
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found			
(AcAc) <sub>3</sub> Ln(Phen)	Eu	40	250–255	51.5	51.5	4.6	4.7	24.2	24.1	N 4.5	4.6		
	Tb	20	250–255	51.0	51.3	4.6	4.7	25.0	25.0	N 4.4	4.5		
(DBM) <sub>3</sub> Eu(Phen)			185–187	68.4	68.4	4.1	4.3			N 2.8	2.8		
(TTFA) <sub>3</sub> Eu(Phen)	75	247–249	43.4	43.7	2.0	2.1	15.3	15.6	F 17.2	17.1	S 9.6	9.7	
(AcAc) <sub>3</sub> Eu(Disty Phen) <sup>c</sup>	86	255–260	61.9	61.9	5.0	5.0	18.3	18.7	N 3.4	3.2			
(TTFA) <sub>3</sub> Eu(Dipy)	32	221–224	42.0	42.4	2.1	2.4	15.6	15.4	F 17.6	17.3	S 9.9	9.6	
(DBM) <sub>3</sub> Eu(Dipy)	17	210–213	67.6	67.6	4.2	4.5			N 2.9	2.8			
(TTFA) <sub>3</sub> Eu(Tripy)	35	247–251	44.8	45.0	2.2	1.9							
(DBM) <sub>3</sub> Eu(Tripy)·C <sub>6</sub> H <sub>6</sub>	67	190–194	70.0	69.9	4.4	4.6	13.4	13.7	N 3.7	3.8			
(TTFA) <sub>3</sub> Eu(PicNO) <sub>2</sub>	35	234–236	41.8	42.3	2.6	2.7			F 16.6	16.8	S 9.3	9.9	
(TTFA) <sub>3</sub> Eu(TPPO) <sub>2</sub>			251–253	52.5	52.6	3.1	3.4	11.0	11.3	F 12.4	12.6	S 7.0	7.0
										P 4.5	4.7		
(TTFA) <sub>2</sub> Ln(TPPO) <sub>2</sub> NO <sub>3</sub>	Eu	44		51.4	51.7	3.2	3.6	12.5	12.8	F 9.4	9.1	S 5.3	5.2
	Tb	61	232–234	51.2	51.4	3.1	3.7	13.0	12.6	P 5.1	5.1	F 9.4	9.7
										S 5.3	5.3		
										P 5.1	4.7		

<sup>a</sup> Abbreviations: AcAc, acetylacetonate; DBM, dibenzoylmethane; TTFA, thenoyltrifluoroacetone; Disty Phen, 4,7-distyrylphenanthroline; Phen, 1,10-phenanthroline; PicNO, 4-picoline N-oxide; TPPO, triphenylphosphine oxide. <sup>b</sup> Prepared by method 6 unless noted. <sup>c</sup> Method 7.

They are difficultly soluble in most common organic solvents and apparently undergo dissociation in solution.

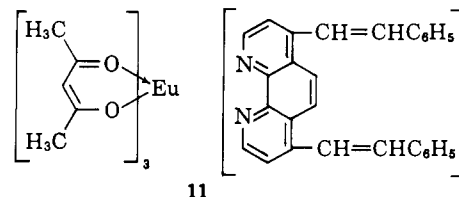


**β-Diketones Complexed with Nitrogen and Oxygen Donors (Table II).**—When an alcoholic solution of hydrated tris(pentane-2,4-dione)europium(III)<sup>2b</sup> was treated with an equimolar amount of 1,10-phenanthroline, the tris(β-diketone)monophenanthroline chelate **10**

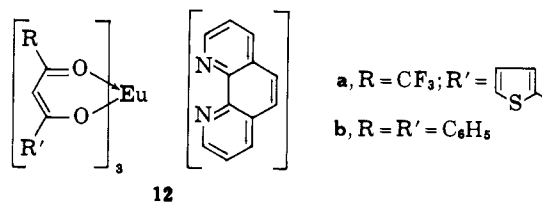


was formed. In the solid state or in solution, the fluorescence of this compound was markedly brighter than that of the parent hydrate. Terbium(III) formed the analog of **10**, but in this case the fluorescence intensities of the hydrate and the phenanthroline compound were qualitatively similar. The distyrylphenanthroline compound **11** was nonfluorescent under similar conditions.

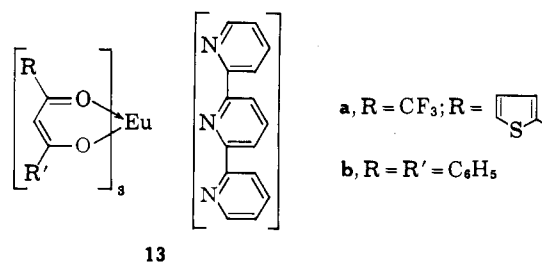
Analogs of **10** with aromatic or fluorine substitution in the β-diketone portion show a marked increase in fluorescence intensity. For example, the thenoyltrifluoro-



acetone- and dibenzoylmethane-phenanthroline chelates **12a** and **12b** are very strongly fluorescent, and the



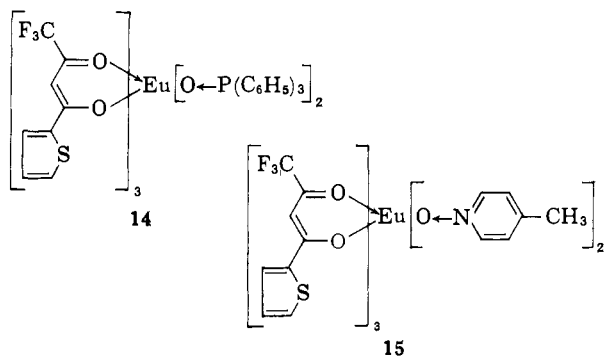
brightness is maintained in solution (e.g., dichloromethane). The use of 2,2'-dipyridyl in place of phenanthroline afforded analogs of **12**, while tripyridyl gave compositions corresponding to **13**. The dibenzoyl com-



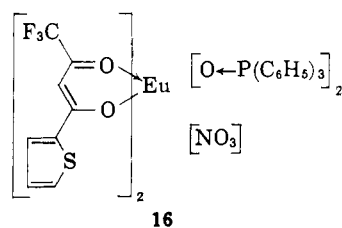
pound **13b** was isolated as the benzene solvate.

Turning to oxide donors, we have isolated complexes corresponding to **14** and **15** from the reaction of europium chloride with the respective ligands and an appropriate base. Ferraro and Healy have reported the

preparation of the neodymium analog of **14**, although they formulate it with only one oxygen atom from each



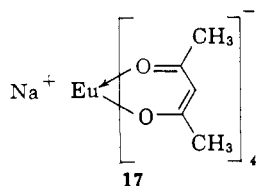
of two diketones bonded to the lanthanide ion.<sup>4</sup> In attempting to prepare **14** from europium nitrate, rather than chloride, we obtained the bis(diketonate) bis(triphenylphosphine oxide) mononitrate **16**, even in the



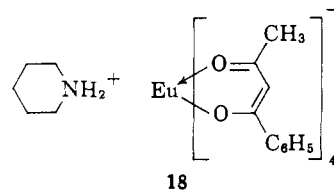
presence of excess triphenylphosphine oxide. The europium compounds **14**, **15**, and **16** are crystalline and are soluble in many organic solvents. They strongly fluoresce as solids and in solution.

**The Anionic Tetrakis( $\beta$ -diketonates) (Table III).**— Previous sections of this paper have described a variety of compounds the compositions of which suggest that rare earth ions commonly occur in an eight-coordinate state. In retrospect, it can be seen that published reports of tris( $\beta$ -diketone) chelates which contain an extra mole of ligand also suggest this property.<sup>1b,17a</sup> Subsequent reports in which preparative procedures similar to those mentioned in ref. 1b and 17 were employed describe benzoylacetone and dibenzoylmethane chelates with compositions corresponding to four  $\beta$ -diketonates, one trivalent lanthanide ion, and one piperidine.<sup>7b,c</sup> Brecher, Lempicki, and Samelson formulate these substances as piperidinium salts of anionic chelates containing a 4:1 ligand-metal ratio.<sup>17c</sup> They also give evidence for eight-coordination of the lanthanide ion. We have independently reached the same conclusion through the preparation and study of the tetrakis salts.

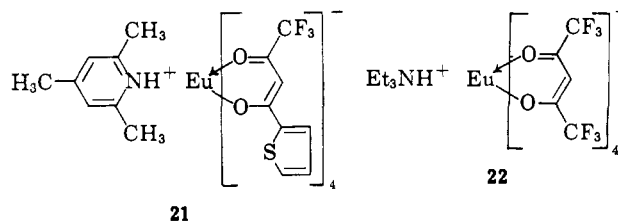
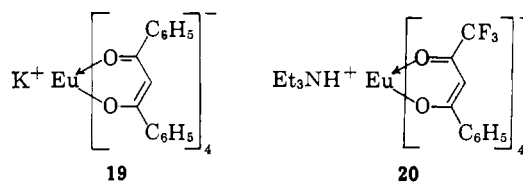
Treatment of hydrated tris(pentane-2,4-diono)europium(III) with sodium acetylacetonate in anhydrous ethanol produced an amorphous, highly insoluble material having the composition of sodium tetrakis(pentane-2,4-diono)europium(III), **17**. A more general route



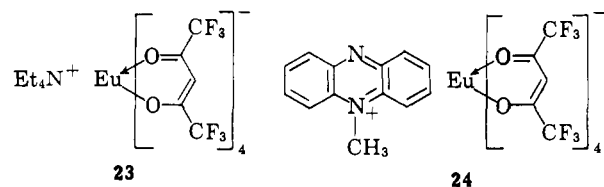
was found in the treatment of a lanthanide(III) salt with 4 or more equiv. each of  $\beta$ -diketone and an appropriate base. Even this route is not universally applicable. For instance, the triethylammonium salt of **17** and **18** could not be isolated using this method and the same conditions which afford the triethylammonium salt of **19**. With the exception of the pentanedione chelates, all of the subsequently described tetrakis compounds were crystalline and appreciably soluble in many organic solvents. For example, the interaction of 4 molar equiv. each of piperidine and benzoylacetone with one of europium chloride afforded the crystalline piperidinium salt, **18**. Other analogous compounds are



illustrated by the salts **19** through **22**. A series of



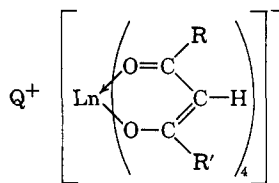
similar chelates was also prepared from salts of eight other rare earths and these are included in Table III. Considerable variation in the cation portion of these salts was achieved by precipitation with quaternary salts as illustrated by the tetraethylammonium and N-methylphenazinium salts **23** and **24**.



Variations in cation and ligand structure were of interest because of their effects on fluorescence intensity and fine structure. Thus, the fluorinated aliphatic chelates showed markedly brighter fluorescence at room temperature than the hydrocarbon chelates. Cations, however, can very effectively quench fluorescence. For example, the solid triethylammonium hexafluoro chelate **22** fluoresces quite brightly yet the N-methylphenazinium salt **25** shows no fluorescence.

Ebullioscopic molecular weight determinations on triethylammonium tetrakis(1,1,1-trifluoro-4-phenylbutane-2,4-diono)europium(III) (**20**) in acetone and in benzene were within experimental error of that calculated for the undissociated salt; thus, in these solvents the compound exists essentially as an ion pair. The

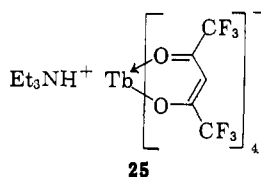
(17) (a) M. Metlay, *J. Chem. Phys.*, **39**, 491 (1963); (b) M. L. Bhaumik, *ibid.*, **40**, 3711 (1964); **41**, 574 (1964); (c) C. Brecher, A. Lempicki, and H. Samelson, *ibid.*, **41**, 279 (1964).

TABLE III  
 TETRAKIS( $\beta$ -DIKETONE) CHELATES


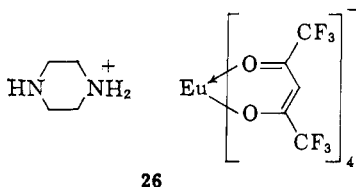
R	R'	Ln	Q <sup>+</sup>	Method	Yield, %	M.p. dec., °C.	% C		% H		% Ln		% Other		
							Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
CH <sub>3</sub>	CH <sub>3</sub>	Eu	Na	8	96	345	42.1	42.0	4.9	5.1			Na	4.0	4.1
CH <sub>3</sub>	CH <sub>3</sub>	Eu	K	9		225	40.9	41.0	4.8	5.0	25.9	25.5	K	6.7	7.3
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	Eu	Na	9	70	220	58.6	58.8	4.4	4.6	18.6	18.1	Na	2.8	2.7
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	Eu	K	9	90		57.5	57.0	4.4	4.4	18.2	18.5	K	4.7	4.6
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	Eu	Piperidinium	10	56	132	61.2	61.3	6.1	5.4	17.2	17.2	N	1.6	1.6
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Eu	Na	11	50	167	67.5	67.2	4.2	4.2	14.2	14.1	Na	2.2	2.0
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Eu	K <sup>a</sup>	11	58	300	66.5	66.8	4.1	4.3	14.0	13.9	K	3.6	3.2
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Eu	Rb	11	70	286	63.8	63.8	3.9	4.0	13.5	13.1	Rb	7.6	6.9
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Eu	Cs	11		280	61.2	60.9	3.8	3.8	12.9	12.6	Cs	11.3	9.9
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Eu	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N	12	70	230	69.5	69.6	5.5	5.6	12.9	12.8	N	1.2	1.2
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Eu	(CH <sub>3</sub> ) <sub>4</sub> N	12		259	68.7	68.3	5.1	5.0	13.6	13.5	N	1.3	1.1
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Eu	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	11		175	69.1	69.0	5.3	5.1	13.3	13.3	N	1.2	1.2
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Eu	Piperidinium	11	45	190	69.0	69.2	5.0	4.7	13.5	13.3	N	1.2	1.2
2-Thienyl	CF <sub>3</sub>	Eu	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	13	93	133	39.9	39.7	2.8	3.3	13.4	13.3	F	20.0	20.2
													S	11.3	11.2
2-Thienyl	CF <sub>3</sub>	Eu	2,4,6-Collidinium	13	23	158	41.5	41.7	2.4	2.6	13.1	13.0	F	19.7	19.4
													S	11.1	11.1
2-Thienyl	CF <sub>3</sub>	Tb	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	13	96	158	39.8	39.3	2.8	3.4	13.9	13.4	F	19.9	19.7
													S	11.2	11.2
2-Thienyl	CF <sub>3</sub>	Tb	Pyridinium	13	54	193	39.2	39.6	2.0	2.3	14.0	13.1	F	20.1	20.4
													S	11.3	11.4
2-Thienyl	CF <sub>2</sub>	Nd	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	13	81	135	40.1	40.4	2.9	3.0	12.8	12.4	F	20.2	20.3
2-Thienyl	CF <sub>3</sub>	La	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	13	64	135	40.5	41.0	2.9	3.1	12.3	11.8	F	20.3	20.3
C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	Eu	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH <sup>b</sup>	13	78	108	49.6	49.1	3.6	4.0	13.7	13.5	F	20.5	20.7
															20.5
C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	Eu	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N	14	50	152	50.0	50.2	3.9	3.6			F	19.9	20.2
C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	Tb	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	13	59	130	49.2	49.2	3.6	3.6	14.1	14.5	F	20.3	20.5
C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	La	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	13	43	130	50.1	50.4	3.7	3.5	12.6	12.3	F	20.6	20.6
C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	Nd	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	13	43	130	49.9	50.4	3.6	3.9	13.0	13.0	F	20.6	20.4
CF <sub>3</sub>	CF <sub>3</sub>	Eu	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH <sup>c</sup>	15	30	130	29.9	29.0	1.8	1.4	14.1	13.9	F	42.1	42.4
CF <sub>3</sub>	CF <sub>3</sub>	Eu	Pyridinium	15	38	175	28.3	28.6	0.9	1.3	14.3	14.6	F	43.0	43.2
CF <sub>3</sub>	CF <sub>3</sub>	Eu	2,6-Lutidinium	15	22	130	29.8	30.2	1.3	1.4	14.0	13.6	F	41.9	42.2
CF <sub>3</sub>	CF <sub>3</sub>	Eu	2,4,6-Collidinium	15	18	130	30.5	30.7	1.5	1.6	13.8	13.8	F	41.4	41.6
CF <sub>3</sub>	CF <sub>3</sub>	Eu	Piperazinium <sup>d</sup>	15	12	210	27.0	27.5	1.4	1.6	14.2	13.8	F	42.8	42.6
CF <sub>3</sub>	CF <sub>3</sub>	Eu	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N	16		153	30.3	30.5	2.2	2.4			F	41.1	41.5
CF <sub>3</sub>	CF <sub>3</sub>	Eu	(CH <sub>3</sub> ) <sub>4</sub> N	16		190	27.4	27.6	1.5	1.8			F	43.3	43.4
CF <sub>3</sub>	CF <sub>3</sub>	Eu	N-Methylquinolinium	16		100	32.0	32.3	1.3	1.5			F	40.6	41.0
CF <sub>3</sub>	CF <sub>3</sub>	Eu	N-Methylphenazinium	16		120	33.7	34.0	1.3	1.5			F	38.8	38.8
CF <sub>3</sub>	CF <sub>3</sub>	Tb	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH <sup>e</sup>	15	28	130	28.7	28.6	1.8	2.0	14.6	14.3	F	41.9	42.1
CF <sub>3</sub>	CF <sub>3</sub>	Tb	Pyridinium	15	30	185	28.2	28.5	0.8	1.2	14.9	14.9	F	42.8	42.4
CF <sub>3</sub>	CF <sub>3</sub>	Tb	2,6-Lutidinium	15	31	130	29.6	29.7	1.3	1.4	14.5	14.5	F	41.6	41.5
CF <sub>3</sub>	CF <sub>3</sub>	Tb	2,4,6-Collidinium	15	39	135	30.4	30.8	1.5	1.6	14.3	14.3	F	41.1	40.9
CF <sub>3</sub>	CF <sub>3</sub>	Nd	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	15	36	130	29.0	29.0	1.9	2.1	13.4	12.9	F	42.7	42.7
CF <sub>3</sub>	CF <sub>3</sub>	Nd	Pyridinium	15	49	185	28.5	28.6	1.0	1.4	13.7	13.2	F	43.3	43.0
CF <sub>3</sub>	CF <sub>3</sub>	Nd	2,6-Lutidinium	15	48	130	30.0	30.5	1.3	1.6	13.4	13.0	F	42.2	42.5
CF <sub>3</sub>	CF <sub>3</sub>	La	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	15	28	130	29.2	29.3	1.9	2.2	13.0	12.5	F	42.6	42.3
CF <sub>3</sub>	CF <sub>3</sub>	La	2,6-Lutidinium	15	47	130	30.2	29.8	1.3	1.5	12.9	12.4	F	42.4	42.4
CF <sub>3</sub>	CF <sub>3</sub>	Pr	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	15	56	130	29.2	28.9	1.9	2.2			F	42.5	42.3
CF <sub>3</sub>	CF <sub>3</sub>	Sm	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	15		130	28.9	29.0	1.9	2.1	13.9	13.7			
CF <sub>3</sub>	CF <sub>3</sub>	Gd	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	15		130	28.8	28.7	1.8	2.2	14.4	14.0			
CF <sub>3</sub>	CF <sub>3</sub>	Dy	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	15		130	28.6	28.5	1.9	2.2			F	41.7	41.7
CF <sub>3</sub>	CF <sub>3</sub>	Ho	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	15		130	28.5	28.4	1.8	2.2			F	41.6	40.5
CF <sub>3</sub>	CF <sub>3</sub>	Er	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	15		130	28.5	28.5	1.8	2.3			F	41.5	41.2
CF <sub>3</sub>	CF <sub>3</sub>	Yb	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH	15		130	28.2	28.0	1.8	2.0			F	41.1	41.4

<sup>a</sup> Mol. wt. Calcd.: 1084. Found: 888, 888 (b.p. in acetone). <sup>b</sup> Mol. wt. Calcd.: 1115. Found: 1090, 1180 (b.p. in benzene), 1040, 1000 (b.p. in acetone); recrystallized from *n*-hexane. <sup>c</sup> Mol. wt. Calcd.: 1082. Found: 828, 793 (b.p. in dichloroethane). <sup>d</sup> Mol. wt. Calcd.: 1067. Found: 380, 376 (b.p. in acetone). <sup>e</sup> Mol. wt. Calcd.: 1039. Found: 920, 908 (b.p. in dichloroethane).

experimentally determined molecular weights of 22 and 25 in dichloroethane were somewhat lower than cal-



culated for the ion pair, suggesting some dissociation. A similar result was obtained for the dibenzoylmethane derivative 19. On the other hand, the piperazinium salt 26 showed a value one-third of that calculated for



an ion pair. This result may be due to dissociation into two ions and a neutral tris chelate.

**Fluorescence Emission Spectra of Europium(III) Complexes.**—There has been much recent interest in the fluorescence of lanthanide complexes<sup>16,5,9,18</sup> and during the course of our work on the synthesis of trivalent europium complexes, we found fluorescence emission spectroscopy to be a valuable characterization aid. That is, combinations of fluorescence emission intensity variations and line shifts imposed by small compositional changes is sufficient, in many cases, to produce an emission spectrum unique to a given complex. This is in contrast to absorption spectroscopy of the lanthanides which oftentimes is not sufficiently inquiring to be helpful.<sup>19</sup> Our interest has been confined mostly to the  $^5D_0 \rightarrow ^7F_0$ ,  $^5D_0 \rightarrow ^7F_1$ , and  $^5D_0 \rightarrow ^7F_2$  transitions of the Eu(III) ion which give rise to the emission of light in the following spectral regions, respectively: 5790–5810, 5850–6000, and 6075–6300 Å.<sup>20</sup> Examples of the effects of compositional changes where the major ligand (in this case, dibenzoylmethane) remains the same throughout a series can be seen in spectra 1–6 of Fig. 1. The addition of 1 mole of water per chelate (spectra 1 and 2) changes the spectrum significantly. The spectrum of the potassium tetrakis chelate (spectrum 3) is essentially identical with those of the rubidium and cesium salts. However, replacement of the alkali metal cation by either the triethylammonium or the tetraethylammonium cation results in quite different spectra (spectra 4 and 5). When a dipyriddy ligand and three dibenzoylmethane groups are present, the spectrum is again unique (spectrum 6). Furthermore, each transition exhibits its maximum multiplicity:  $^5D_0 \rightarrow ^7F_0$ , one line;  $^5D_0 \rightarrow ^7F_1$ , three lines; and  $^5D_0 \rightarrow ^7F_2$ , five lines. The line arising from the  $^5D_0 \rightarrow ^7F_0$  transition has particular value. In all symmetries, it must be a singlet. The occurrence of more than one line in this spectral region therefore indicates the presence of more than one Eu(III) site and would thus suggest the presence of isomers or a mixture of europium complexes.

(18) H. Samelson, A. Lempicki, V. A. Brophy, and C. Brecher, *J. Chem. Phys.*, **40**, 2547 (1964).

(19) See ref. 7 for leading references to effects of chelating agents on lanthanide absorption bands.

(20) G. H. Dieke, H. M. Crosswhite, and B. Dunn, *J. Opt. Soc. Am.*, **51**, 820 (1961).

We have found that complexes of monodentate ligands are also distinctive. The iodide, perchlorate, and hexafluorophosphate salts of the octakis(4-picoline N-oxide)europium(III) cation are all similar (spectrum 7), but easily distinguished from the tris(N- and P-oxide) complexes of europium trichloride (spectra 8 and 9).

Effects of solvents on the spectra are quite diverse. The spectrum of potassium tetrakis(1,3-diphenyl-1,3-propanedion)europium(III) in dichloromethane is quite sharp and somewhat similar to that of the solid (spectra 10 and 3). However, emission spectra at room temperature of alcoholic solutions of most of the chelates exhibit band emission with few characterizing lines. For example, the spectrum of piperidinium tetrakis(1-phenyl-1,3-butanediono)europium(III) in alcohols at room temperature is weak and diffuse compared to that of the solid (spectra 11 and 12). Cooling of the solution to  $\sim 77^\circ\text{K}$ . results in marked brightening, as well as the emergence of a well-defined, sharp-line spectrum which, however, is distinguishable from that of the solid (spectra 13 and 12). A similar temperature effect was previously described by Samelson and co-workers.<sup>18</sup>

Spectrum 14 is of the same solution used for spectrum 13, except that it had been allowed to stand at room temperature in a closed container for 43 days. This example illustrates the potential use of fluorescence emission spectra for monitoring chemical changes.

### Experimental

**Fluorescence Emission Spectrum Apparatus.**—The first-order fluorescence emission spectra were obtained with a Leeds and Northrup Model 6750-A1 recording spectrometer.<sup>21</sup> This instrument uses a 3-in. grating with 30,000 lines/in. in an Ebert mounting and has a first-order spectral resolution of 0.1 Å. An RCA 1P28 photomultiplier tube placed behind the exit slit served as a detector. Since the wave-length drive of the spectrometer is linear in time, accurate recording of spectra can be made with a strip chart recorder. The measured fluorescence was excited by the light from an AH3 mercury lamp filtered by a Corning C.S. 7-37 filter (resulting in primarily 3660 Å. radiation) and focused on a  $\sim 2$ -mm. layer of the solid sample contained in the bottom of a 15 × 15 mm. screw-cap vial. The solutions were contained in similar vials which could be immersed in liquid nitrogen. A Corning C.S. 3-71 filter placed in front of the entrance slit of the spectrometer excluded stray ultraviolet light from the mercury lamp which might otherwise be detected in second order.

The spectra exhibited here show the relative photomultiplier signal as a function of wave length and are sufficient for characterization purposes. Relative fluorescent intensities can be obtained by correcting for the spectral response characteristics of the entire spectrometer system.

The complexes were prepared as described below. Commercially available solvents of reagent grade or better were used as received, with no further purification. The solutions were filtered through sintered glass frits prior to measuring emission spectra.

**Synthesis.**—Europium chloride stock solution was prepared by suspending 8.8 g. of anhydrous europium oxide (99.99% pure)<sup>22</sup> in 150 ml. of 1 N hydrochloric acid and digesting on a steam bath until completely dissolved. The solution was made up to a volume of 250 ml. and filtered; the concentration was 2 mmoles of europium chloride per 10 ml. Nitrate salt solutions of similar concentrations were prepared by dissolving the commercial nitrates (99.99% pure) in water. Other reagents were the best obtainable commercial grade material and were used without further purification.

Unless otherwise noted, the products were dried under high vacuum, at room temperature, over phosphorus pentoxide for 24 hr.

**Methods of Preparation.**—The preparations detailed here are prototype reactions. The method for any particular compound

(21) W. G. Fastie, *ibid.*, **42**, 641 (1952); **42**, 647 (1952).

(22) Lindsay Chemical Division, American Potash and Chemical Corp., West Chicago, Ill.

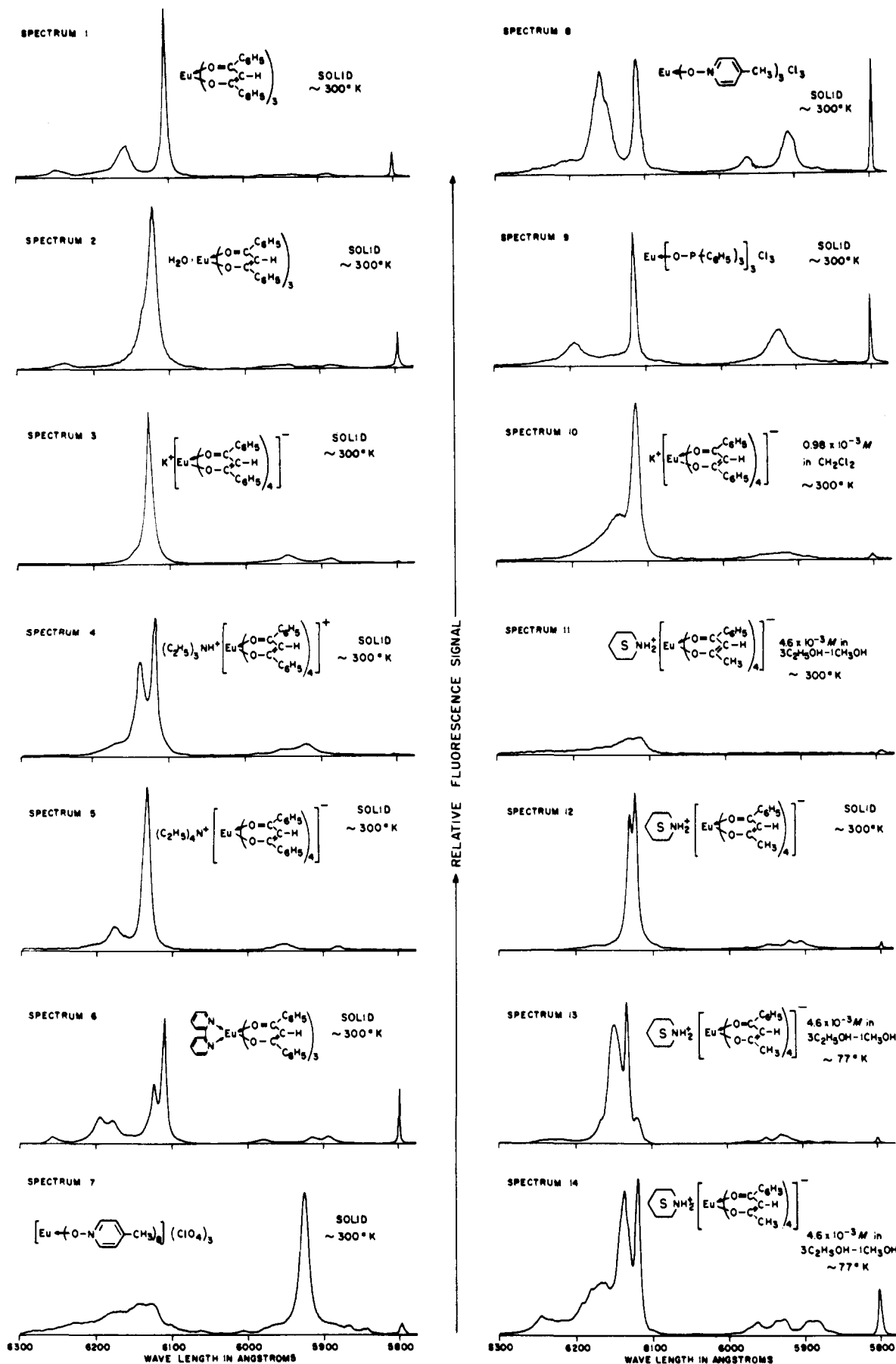


Fig. 1.—Fluorescence emission spectra (3660 Å. excitation) of various europium(III) complexes.

in the tables is indicated by a numeral corresponding to one of these examples.

1. Tris(4-picoline N-oxide)europium(III) Chloride.—Europium oxide (0.7 g., 2 mmoles) was dissolved in 12 ml. of 1 *N*

hydrochloric acid, and 3.5 g. (32 mmoles) of 4-picoline N-oxide was added. The mixture was evaporated to dryness and taken up in 15 ml. of hot ethanol; the solution was filtered and treated with 60 ml. of ethyl acetate to precipitate fine white needles. In other related preparations, acetone was used as the precipitant.

**2. Octakis(4-picoline N-oxide)europium(III) Perchlorate.**—To 4 mmoles of europium perchlorate in 20 ml. of water was added 3.5 g. (32 mmoles) of 4-picoline N-oxide. The solution was heated and filtered, and 300 ml. of isopropyl alcohol was added to the filtrate. The solution was evaporated on a steam bath until cloudy, then cooled to obtain a semisolid mass. The solid was isolated on a filter and dissolved in 35 ml. of hot acetone; the solution was filtered and treated with about 10 ml. of ethyl acetate. The mixture was cooled in a Dry Ice-acetone mixture to obtain 1.15 g. of white platelets. This product was further purified by precipitation from acetone (25 ml.) with ethyl acetate.

**3. Octakis(4-picoline N-oxide)europium(III) Hexafluorophosphate.**—A solution containing 0.98 g. (6 mmoles) of ammonium hexafluorophosphate, 2.2 g. (20 mmoles) of 4-picoline N-oxide, and 2 mmoles of europium chloride in 10 ml. of water was evaporated to dryness at room temperature under a nitrogen stream. The solid was taken up in 50 ml. of boiling acetone, the mixture filtered, and 75 ml. of ether added to the filtrate to obtain a crystalline solid. The reprecipitation procedure was repeated.

**4. Phenanthroline and Tripyridyl Lanthanide(III) Salts.**—A solution of 4 mmoles of *o*-phenanthroline or tripyridyl in 50 ml. of 95% ethanol and 2 mmoles of the rare earth salt in 10 ml. of water was heated to boiling, filtered, and treated with 150 ml. of boiling acetone. The solution was allowed to stand at room temperature for two days and deposited the crystalline, analytically pure chelate. In the case of the tripyridyl-terbium nitrate product, ether (500 ml.) was added to the ethanol-acetone solution to cause precipitation.

**5. Tris(1,1,1-trifluoro-4-(2-thienyl)-2,4-butanediono)aqueo-europium(III).**—In 15 ml. of 95% ethanol was dissolved 3 mmoles of  $\beta$ -diketone, and then 3 ml. of 1 *N* sodium hydroxide and 1 mmole of europium chloride in 5 ml. of water were added. An additional 100 ml. of water was added and the mixture was heated to 60° and then stirred until cooled to room temperature. The solid was collected and dissolved in 30 ml. of warm benzene (40°), and 100 ml. of *n*-hexane was added. The mixture was allowed to stand at room temperature overnight, and the product was collected and air-dried at room temperature; yield 15%, m.p. 134–140°. The infrared absorption spectrum showed a band at 3  $\mu$  assigned to the water of hydration.

*Anal.* Calcd. for  $C_{24}H_{14}EuF_9S_3O_7$ : C, 34.6; H, 1.7; F, 20.5; S, 11.5; Eu, 18.3. Found: C, 34.4; H, 2.1; F, 20.0; S, 11.2; Eu, 18.7.

**6. Tris(propene-1,3-diono)(monophenanthroline)europium(III).**—In 20 ml. of hot 95% ethanol 6 mmoles of  $\beta$ -diketone and 2 mmoles of neutral ligand were dissolved, and 6 ml. of 1 *N* sodium (or potassium) hydroxide was added. The mixture was stirred while 2 mmoles of rare earth salt solution was added dropwise. The mixture was cooled, and in most cases the product was collected and recrystallized from 95% alcohol using Celite Filter-Aid. However, the dibenzoylmethane-phenanthroline and -tripyrindyl compounds were purified by dissolving in benzene (30 ml.) and precipitating with 30 ml. of hexane.

**7. Tris(2,4-pentanediono)(4,7-distyrylphenanthroline)europium(III).**—In 200 ml. of boiling toluene were dissolved 1.2 mmoles of europium tris(acetylacetonate) trihydrate and 1.28 mmoles of 4,6-distyrylphenanthroline. About 50 ml. of solvent was distilled out and the hot solution was filtered and allowed to stand overnight to obtain yellow needles.

**8. Sodium Tetrakis(2,4-pentanediono)europium(III).**—In a boiling mixture of 75 ml. of absolute ethanol and 15 ml. of benzene was dissolved 1.34 g. (2.87 mmoles) of europium(III) tris(acetylacetonate) monohydrate. To this hot solution was added dropwise a solution of sodium acetylacetonate prepared from 20 ml. of ethanol, 0.07 g. (3.05 g.-atoms) of sodium, and 0.305 g. (3.05 mmoles) of acetylacetonate. An additional 30 ml. of ethanol and 20 ml. of benzene were added, and then 50 ml. of liquid was removed by distillation. The solid was collected and air-dried, yield 1.56 g. (96%). It was continuously extracted (Soxhlet apparatus) with ethanol for 2.5 hr.

**9. Sodium Tetrakis(1-phenyl-1,3-butanediono)europium(III).**—Benzoylacetone (1.62 g., 10 mmoles) was dissolved in a mixture of 50 ml. of acetone and 10 ml. of 1 *N* alkali hydroxide. The

mixture was heated to reflux and 2 mmoles of europium chloride in 10 ml. of water was added. The solution was gravity filtered while hot and the filtrate was allowed to cool to room temperature. The needles were collected on a filter and washed with acetone-water (1:1).

**10. Piperidinium Tetrakis(1-phenyl-1,3-butanediono)europium(III).**—In a boiling mixture of 20 ml. of ethanol and 0.79 ml. (8 mmoles) of piperidine was dissolved 1.3 g. (8 mmoles) of benzoylacetone. Europium chloride (2 mmoles in 10 ml. of water) was added to the refluxing solution, and the mixture was allowed to stand at room temperature for 24 hr. The solid mixture was collected on a filter, and the crystalline portion was mechanically separated and dried as above.

**11. Alkali Salts of Tetrakis(1,3-diphenyl-1,3-propanediono)europium(III).**—Dibenzoylmethane (1.79 g., 8 mmoles) was dissolved in a mixture of 25 ml. of ethanol and 16 ml. of 0.5 *M* aqueous base solution. To this solution was added 2 mmoles of europium chloride in 10 ml. of water. The mixture was cooled in ice water and the solid was collected on a filter. The product was dissolved in 200 ml. of *o*-dichlorobenzene heated on a steam bath, the solution was filtered, and the filtrate was cooled to obtain yellow needles of the purified product.

**12. Alkylammonium Salts of Tetrakis(1,3-diphenyl-1,3-propanediono)europium(III).**—Dibenzoylmethane (1.79 g., 8 mmoles), tetraethylammonium chloride monohydrate (0.45 g., 3 mmoles), 25 ml. of ethanol, and 8 ml. of 1 *N* sodium hydroxide were heated on a steam bath until all solids had dissolved. To this warm solution was added 2 mmoles of  $EuCl_3$  in 10 ml. of water. The solid was collected, washed with water, and recrystallized twice from 100 ml. of *o*-dichlorobenzene.

**13. Salts of Tetrakis(1,1,1-trifluoro-4-aryl-2,4-butanediono)lanthanide(III).**—In 60 ml. of boiling 95% ethanol was dissolved 18 mmoles of  $\beta$ -diketone, and 18 mmoles of amine was added. The solution was heated to boiling and 4 mmoles of rare earth salt in 20 ml. of water was added, the solution heated again to boiling and filtered hot. In some instances the chelate began separating as an oil during the initial phase of cooling in which case crystallization was induced either by gentle swirling of the cloudy solution or by brief scratching of the inner surface of the flask with a glass rod. The mixture was allowed to stand overnight at room temperature to afford analytically pure, crystalline chelate.

**14. Tetraethylammonium Tetrakis(1,1,1-trifluoro-4-phenyl-2,4-butanediono)europium(III).**—In 50 ml. of 95% ethanol was placed 4.32 g. (20 mmoles) of benzoyltrifluoroacetone and 1.1 g. (5 mmoles) of tetraethylammonium bromide. The mixture was heated to boiling, 20 ml. of 1 *N* NaOH was pipetted in, and then a solution of 2.2 g. (5 mmoles) of europium nitrate hexahydrate in 20 ml. of warm water was added. The mixture was allowed to stand at room temperature for 2 days; the crystalline product was collected on a filter, washed with 50% alcohol, and dried.

**15. Ammonium Salts of Tetrakis(1,1,1,5,5,5-hexafluoro-2,4-pentanediono)lanthanide(III).**—To 50 ml. of 95% ethanol was added 20 mmoles of amine, 3.6 ml. of hexafluoroacetylacetone, and a solution of 5 mmoles of lanthanide nitrate hexahydrate in 25 ml. of water. The solution was boiled down to half of its original volume, and 100 ml. of water was added to precipitate a sticky solid. Vigorous scratching converted it to a granular product which was collected on a filter, washed with water, and air-dried. It was recrystallized from chloroform.

**16. Quaternary Salts of Tetrakis(1,1,1,5,5,5-hexafluoro-2,4-pentanediono)lanthanide(III).**—To 50 ml. of 95% alcohol was added, in this specific order, 20 ml. of 1 *N* sodium hydroxide, 3.2 ml. of hexafluoroacetylacetone, then a solution of 2.2 g. of europium nitrate hexahydrate in 20 ml. of water, and finally a solution of 10 mmoles of quaternary ammonium halide or methylsulfate in 10 ml. of water. The solution was concentrated by boiling on a steam bath until crystallization began, then just sufficient ethanol was added to dissolve the solid at the boiling point. The solution was gravity filtered and allowed to stand overnight at room temperature to afford analytically pure, crystalline chelate.

**17. Tris(1,3-diphenyl-1,3-propanediono)aqueo-europium(III).**—To a refluxing mixture of 1.3 g. (6 mmoles) of dibenzoylmethane, 48 ml. of acetone, and 12 ml. of 0.5 *N* potassium hydroxide was added 2 mmoles of europium chloride in 10 ml. of water. The solution was filtered and cooled to obtain yellow needles, yield 60%, m.p.  $\sim 210^\circ$  dec.



*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  $110^\circ$ , 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.

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## Octacoordinate Chelates of Lanthanides. Two Series of Compounds

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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( $\beta$ -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.<sup>2-4</sup> The most widely studied of these chelates have been those having  $\beta$ -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 matrix<sup>1</sup> and with 1-phenyl-1,3-butanedione (PBD) in alcoholic solutions.<sup>3,5,6</sup> An inspection of the majority of the many publications describing studies of the spectroscopic properties of lanthanide  $\beta$ -diketonone chelates<sup>7-21</sup> 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 Alire<sup>12</sup> 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 Crosby<sup>22</sup> 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<sup>5,15-18,20</sup> 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. Metlay<sup>23</sup> 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 suggested<sup>24</sup> to explain similar behavior for the product obtained from europium and PBD by the "piperidine method" ( $EuB_4$ ). Ohlmann and Charles<sup>25</sup> have also discussed  $EuD_3$  and pointed out the possibility that " $EuD_4$ " might also contain piperidine. Winston and co-workers<sup>26</sup> 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.<sup>6,27</sup>

Until recently, the trivalent lanthanide ions were thought to be hexacoordinate in their reactions with various chelating ligands, and a number of tris( $\beta$ -diketonon)lanthanide(III) compounds have indeed been prepared and characterized.<sup>28-31</sup> 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. Nucl. Chem.*, **26**, 373 (1964).
- (31) F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **40**, 2790 (1964).