

XXVI.* METALLOATRAN-3,7,10-TRIONES CONTAINING
RARE-EARTH-ELEMENT HETEROATOMS

M. G. Voronkov and S. V. Mikhailova

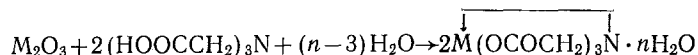
UDC 547.79'256.5

Methods for the preparation of metalloatran-3,7,10-trione hydrates (containing rare-earth-element heteroatoms) of the $\overline{N(CH_2COO)_3M} \cdot nH_2O$ type ($M = La, Ce, Nd, Eu, Gd, Dy, Ho, Er, Yb$) are described. Their IR spectra and derivatograms were studied.

Continuing our investigation of chelate compounds of metals with amino acids (which we have arbitrarily named metalloatran-3,7,10-triones), we have turned our attention to the corresponding derivatives of the rare-earth elements (REE) of the $\overline{N(CH_2COO)_3M}$ type ($M = REE$). Nitrilotriacetic acid (I) has been used for many years to separate REE mixtures [2-7]. The formation of complexes of europium with I was studied by paper electrophoresis [8]. Complexes of I with lanthanum were obtained and described [9], and their stability constants were determined [10-15]. Complexes of I with Gd, Nd [13, 14, 16, 17], and Ce [18] have also been investigated. It has been pointed out that the titration curve of the complex of I with Gd differs in character from those for the remaining REE [11].

The preparative methods, structures, and properties of REE complexes with I have been described most completely in [12-17].

We have obtained the hydrates of nine metalloatran-3,7,10-triones (which contain an REE heteroatom) of the $\overline{N(CH_2COO)_3M} \cdot nH_2O$ (II) type, where $M = La, Ce, Eu, Gd, Nd, Ho, Er$, and Yb (Table 1), by reaction of the appropriate REE oxides with I in water.



* See [1] for communication XXV.

TABLE 1.

M	n	Empirical formula	$\overline{N(CH_2COO)_3M} \cdot nH_2O$				Yield, %			
			Found, %				Calc., %			
			C	H	N	M	C	H	N	M
La	3	$C_6H_{12}NO_9La$	18,84	3,12	6,64	36,55	18,91	3,17	3,67	36,45
Ce	3	$C_6H_{12}NO_9Ce$	19,46	2,82	3,07	36,60	18,90	2,90	3,67	36,76
Nd	3	$C_6H_{12}NO_9Nd$	18,97	3,72	3,31	37,00	18,63	3,13	3,63	37,34
Eu*	3	$C_6H_{12}NO_9Eu$	18,72	3,19	3,50	39,50	18,30	3,05	3,56	38,50
Gd	5	$C_6H_{16}NO_{11}Gd$	16,75	3,65	3,24	36,70	16,50	3,68	3,22	36,05
Dy*	5	$C_6H_{16}NO_{11}Dy$	16,90	3,86	3,34	37,40	16,40	3,64	3,18	36,90
Ho	3	$C_6H_{12}NO_9Ho$	17,68	3,05	3,32	40,80	17,75	2,96	3,44	40,50
Er	2	$C_6H_{10}NO_8Er$	18,95	2,80	4,11	43,00	18,40	2,56	3,58	42,80
Yb*	6	$C_6H_{18}NO_{12}Yb$	15,48	3,58	2,80	36,20	15,35	3,74	2,99	36,90

* New compound.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 5, pp. 610-613, May, 1971. Original article submitted November 9, 1969.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 2. Frequencies of the Absorption Maxima in the IR Spectra
of $N(CH_2COO)_3M \cdot nH_2O^*$

La	Ce	Eu	Gd	Dy	Ho	Er	Yb
413 m		425	425		425	425	
494 m	482s	490		490			
562 m	541m	510	510		515	515	
	580w		570		575		
		620	620	620	625	620	625
				585			708 w
722 s	744s	735 s	741 m	740 m	743 m	742 m	732 m
				775 w			746 m
	866w	838 vw	841 w	864 w	850 w		
		875 vw		904 m			
912 s	902m	914 w	914 m	913 m	915 s	916 s	917 s
995 m	966m	930 w	932 m	930 m	934 m		934 m
		997 w	994 m	971 m	952 w		
					975 w	973 s	997 w
	1009m	1006 w	1027 m	1015 m	1014 w	1017 m	1020 m
			1100 w	1025 w	1027 m	1024 m	1094 w
1122	1120	1133 m	1134 m	1127 m	1128 s	1133 m	1133 m
			1186 w				
1242 w	1200s	1209 w	1233 w	1236 w	1230 w		1240 w
	1236s	1233 w		1255 s			
		1272 m	1272 m	1272 m	1270 m	1270 s	1276 m
1306 m		1318 m	1318 m		1315 s	1317 m	1322 m
1335 m	1325m	1346 s	1349 s	1341 m	1342 s	1346 m	1347 m
		1366 m	1366 m	1387 s	1363 m		1367 m
	1406m	1400 m		1397 m	1400 m	1401 w	
	1430m	1422 s	1424 s	1419 s	1420 s	1423 s	1426 s
		1435 s	1435 m	1433 s	1448 s	1436 s	1440 s
		1454 s	1452 s			1460 m	1453 s
							1463 w
		1477 s	1471 s	1473 m	1474 s	1476 m	1479 s
	1574s			1480 m		1490 w	1490 w
		1608 vs	1595 vs	1600 vs	1604 vs	1600 vs	16014 vs
	1723s	2243 w		2252 w	2240 w		2270 w
		2320 w	2330 w	2370 m	2380 w	2351 w	2330 w
			2851 s			2852 m	2385 w
		2920 m	2918 vs	2923 s	2920s	2923 s	2855 w
						2953 m	2930 m
		3206 s	3180 m	3033 s	3103 s	3167 s	3050 s
				3155 s			
			3340 m	3360 s		3340 s	
		3490 s			3452 s		3450 s
					3572s		
		3580 s	3580 w	3575 m	3575 s	3580 m	3580 m

*In cm^{-1} ; m is medium, s is strong, w is weak, vs is very strong, and vw is very weak.

We previously [19] described II with $M = La, Ce$, and Nd , while II with $M = Eu$ and Dy were obtained for the first time. (Structure II with $M = La$ [9, 12], Pr, Nd, Y, Yb [12], Sm, Er [12, 15], Gd [12, 13], and Ho [13] have been reported.)

We obtained II with $M = Yb$ as the trihydrate. It was previously [12] pointed out that it exists only as the tetrahydrate.

All of the II obtained are white, crystalline substances (except II with $M = Eu$ and Nd , which are rose-colored) which are only slightly soluble in water (except for II with $M = La$, which is not at all soluble).

We studied the IR spectra of all of the II from 400 to 4000 cm^{-1} (Table 2). (Up to now the spectra of II with $M = La, Pr, Nd, Sm, Gd, Y, Er$, and Yb from 1600 to 1650 cm^{-1} have been studied.) The spectra of all II contain an absorption band at 510 cm^{-1} , which we assigned to the vibration of the $M \leftarrow N$ bond. The formation of this bond is also indicated by the shift in the spectra of II of the band of the valence vibration of the $C-N$ bond to the low-frequency region ($1120-1134\text{ cm}^{-1}$) as compared with the sodium and potassium salts of I (1147 cm^{-1} , respectively).

The presence of a strong absorption at $1620-1650\text{ cm}^{-1}$ ($\nu_{as}\text{ COO}^-$) and at $1420-1450\text{ cm}^{-1}$ ($\nu_s\text{ COO}^-$) as well as the absence of a band at $1700-1750\text{ cm}^{-1}$ ($\nu\text{ C=O}$) indicate the ionic character of the bonds of all three COO groups with the metal as well as their equivalency. These data make it possible to conclude that

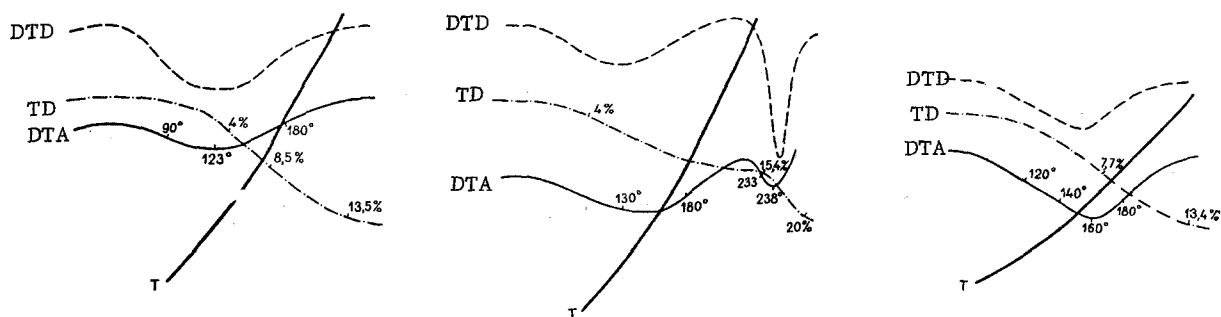


Fig. 1. Derivatograms of metalloatran-3,7,10-triones containing REE heteroatoms (heating rate 12 deg/min): T) heating curve; TD) thermo-gravimetric curve; DTA) differential heating curve; DTD) derivative curve.

the compounds obtained actually have the metalloatran-3,7,10-trione hydrate structure, in which the endocyclic M-O bonds have ionic character.

A single broad band, which was assigned to the vibrations of the O-H bond of water, is observed at $3000-3500\text{ cm}^{-1}$ in the spectra of compounds with $M = \text{Gd}$ and Yb . At the same time there are two or three bands in this region in the spectra of the remaining II. This indicates that not all of the water molecules are identically bonded to the metalloatran-3,7,10-trione molecule (see also [12]).

A study of the derivatographic curves (Fig. 1) of the thermal decomposition of the compounds indicates that they all lose all of their water of hydration up to $180-240^\circ$, and above this temperature they decompose to form M_2O_3 . Compound II with $M = \text{Eu}$ begins to decompose at 90° . The trend of the heating curve indicates the presence of an endothermic effect at 160° which is accompanied by the loss of two water molecules. On further heating to 180° it loses yet another water molecule. Above 180° rapid decomposition of the compound accompanied by combustion is observed. The white residue after combustion of the organic part of the compound is Eu_2O_3 . Two endothermic effects at 130 and 238° are observed during the thermal decomposition of II with $M = \text{Dy}$. The attendant weight loss corresponds to the loss of two and five water molecules (the last five water molecules are lost at 235°). Above 238° the substance decomposes completely to form Dy_2O_3 .

Compound II with $M = \text{Yb}$ contains six molecules of water of crystallization, three of which are lost on heating from 123 to 180° .

EXPERIMENTAL

Analytical grade nitrilotriacetic acid (I) recrystallized from hot water was used. The starting REE oxides were also analytical grade reagents. The IR spectra were obtained with a UR-10 spectrometer (KBr prism) and an IKS-14 spectrometer (NaCl and LiF prisms). The spectra were obtained from suspensions of the solid hydrates in mineral oil. The derivatograms were obtained with a derivatograph [20].

A list of the five methods used to synthesize the metalloatran-3,7,10-triones containing an REE heteroatom (II) is given below.

- 1) An equimolar amount of I and the appropriate REE oxide were mixed with excess water at room temperature and shaken for 4 h. After all of the oxide dissolved, the solution was filtered, and all of the water was removed from it in a rotary vacuum evaporator. The residue was suspended in absolute alcohol, suction filtered, and dried in vacuo.
- 2) A mixture of equimolar amounts of I and the REE oxide was refluxed with excess water for 2 h (until the material went into solution). The hot solution was filtered, the water was removed from it in a rotary vacuum evaporator, and the residue was suspended in absolute alcohol, suction filtered, and dried in vacuo.
- 3) An aqueous solution of an REE salt was poured into a hot aqueous solution of an equimolecular amount of I. The solution was slowly evaporated to half its original volume. The crystals of II that precipitated on cooling were suction filtered, washed with hot water, alcohol, and ether and vacuum dried.

4) Aqueous solutions of equimolecular amounts of an REE salt and I were mixed, and the precipitate of II was suction filtered, washed with hot water, alcohol, and ether and vacuum dried.

5) Aqueous solutions of equimolecular amounts of an REE salt and trisodium nitrilotriacetate were mixed. The precipitate of II that formed on standing was suction filtered, washed with hot water, alcohol, and ether and vacuum dried.

LITERATURE CITED

1. V. A. Pestunovich, M. G. Voronkov, G. I. Zelchan, A. F. Lapsin', É. Ya. Lukevits, and L. I. Libert, *Khim. Geterotsikl. Soedin.*, No. 2, 348 (1970).
2. R. V. Kotlyarov and G. P. Kozhemyako, *Rare Earth Elements* [in Russian], *Inst. Geokhim. i Anal. Khim.*, Akad. Nauk SSSR (1959), p. 62.
3. G. Beck and A. Gasser, *Anal. Chim. Acta*, 3, 41 (1949).
4. L. Holleck and D. Eckardt, *Z. Naturforsch.*, 9, 347 (1954).
5. L. Wolf and J. Massone, *Chem. Technol.*, 10, 290 (1958); *J. Prakt. Chem.*, 5, 288 (1958).
6. G. Beck, *Helv. Chim. Acta*, 29, 357 (1946).
7. G. Beck, *Microchim. Acta*, 33, 344 (1948).
8. G. Marcu, M. Thomus, and M. Solea, *Stud. Univ. Babes-Bolyai, Chem.*, 13, 11 (1938).
9. D. I. Ryabchikov and E. K. Korchemnaya, *Rare Earth Elements* [in Russian], *Inst. Geokhim. i Anal. Khim.*, Akad. Nauk SSSR (1963), p. 141.
10. G. Anderegg, *Helv. Chim. Acta*, 43, 825 (1960).
11. G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, 39, 1589 (1956).
12. N. D. Mitrofanova, L. I. Marynenko, and A. I. Grigor'ev, *Zh. Neorgan. Khim.*, 9, 320 (1964).
13. N. Brintzinger, H. Thiele, and S. Munkelt, *Z. Anorg. Chem.*, 254, 271 (1947).
14. Z. F. Andreeva and A. S. Kostygov, *Rare Earth Elements* [in Russian], *Izd. Akad. Nauk SSSR, Moscow* (1959), p. 108.
15. G. Schwarzenbach, *US Patent No. 3,107,259* (1963); *Chem. Abstr.*, 60, 3758 (1964).
16. N. S. Vagina and Yu. Liang-Yang, *Zh. Neorgan. Khim.*, 6, 1569 (1961).
17. K. F. Belyaeva, M. A. Porai-Koshits, N. D. Mitrofanova, and L. I. Martynenko, *Zh. Strukt. Khim.*, 7, 130 (1966); 9, 541 (1968).
18. V. B. Verenikin and K. V. Astakhov, *Zh. Neorgan. Khim.*, 10, 2753 (1965).
19. M. G. Voronkov and S. V. Mikhailova, *Khim. Geterotsikl. Soedin.*, 49 (1969).
20. F. Paulik, J. Paulik, and L. Erdey, *J. Anal. Chem.*, 160, 241 (1958).