ATRANES

XIX. Metalloatrane-3,7,10-triones Derived from Multivalent Metals*

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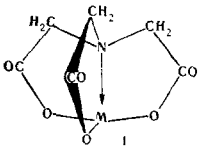
General methods are described for the preparation of metalloatrane-3,7,10-triones $N(CH_2COO)_3M$, containing an atom of a ter-, quarter-, or quinquevalent metal (mainly in the form of hydrates). Seven intramolecular compounds of this type (with M = Nd^{III}, $ClTi^{IV}$, $ClZr^{IV}$, Ce^{III}, $HOPb^{IV}$, $HOMn^{IV}$, $HOOU^{VI}$), have been prepared, of which only two (with M = Nd^{III} and $HOOU^{VI}$) were known previously. Compounds with the composition $N(CH_2COO)_3M \cdot mN(CH_2COO)_3 \cdot nH_2O$ with M = Nd^{III}, Th^{IV}, Co^{III} and Ni^{III} (m = 1) and with M = Sb (m = 3 and 4) have also been obtained.

We have previously obtained internally complex metal derivatives of nitrilotriacetic acid—metalloatrane-3,7,10-triones $N(CH_2COO)_3M$, in which M is an atom of a tervalent metal (Al, Ga, In, La, Tl, Bi, Fe, Co, Ni) [2]. It then appeared of interest to synthesize internally complex salts of this acid of similar structure of type I containing an atom of a quater- or a quinquevalent metal.



In formula I, M represents a group of atoms containing an atom of a multivalent metal which may be coordinately bound with molecules of water and other ligands.

Up to the present time, only complex compounds of nitrilotriacetic acid of this type containing Th^{IV} [3] and U^{VI} [4] have been isolated in the individual state. At the same time, it is impossible not to observe that the capacity of nitrilotriacetic acid (II) for forming complexes with ions of multivalent metals is widely used in analytical practice [5–7].

The capacity of II for forming complexes with ions of Nd^{III} [8,9], Ce^{IV} [10], Ti^{IV} [11–13], Zr^{IV} [14–21], Th^{IV} [22–25], and U^{VI} [26–29] has been studied by various methods.

In this paper we describe four general methods for the synthesis of I. Using these methods we have obtained a number of compounds of this type with M = = $ClTi^{IV}$, $ClZr^{IV}$, Ce^{III}, $HOPb^{IV}$, and $HOOU^{IV}$. All these compounds were isolated in the form of hydrates containing 2–7 molecules of water.

The reaction of II with $TiCl_4$ (in dimethylformamide) and $ZrCl_4$ (or $ZrOCl_2$) in water smoothly forms the corresponding 1-chlorometalloatrane-3,7,10-triones (M = $ClTi^{IV}$ or $ClZr^{IV}$). Compounds with M = $HOPb^{IV}$ and $HOMn^{IV}$ are obtained by the reaction of II with PbO_2 and MnO_2, respectively. Compounds with $HOOU^{IV}$ are prepared by the reaction of II with $(CH_3COO)_2UO_2$ (in an aqueous medium). In addition, supplementing results obtained previously, the reaction of II with $NdCl_3$ in an aqueous medium gave yet another compound of type I in which M is an atom of a tervalent metal. This compound (with M = Nd^{III}), isolated in the form of the trihydrate, has been described previously [3].

The method of preparation, yields, and analytical data, colors, and solubilities of all the I obtained are given in Table 1. The structure of these compounds, for which we propose formula I at the present time, will be refined later with the aid of physical and chemical methods of investigation.

In the reaction of II in aqueous solution with $ThCl_4$, $SbCl_3$, CoO(OH), and NiO(OH), it is not compounds of type I that are formed but complexes containing from two to five residues of II per metal atom, with the composition $N(CH_3COO)_3M \cdot mN(CH_3COOH)_3 \cdot nH_2O$ (Table 2). The question of whether these compounds are complexes of the corresponding metalloatrane-3,7,10-triones with II or acid salts with a different structure will be considered subsequently.

EXPERIMENTAL

Initial reactants. Chemically pure salts of the multivalent metals with volatile acids (chlorides, acetates) or freshly-precipitated hydroxides and oxides and nitrilotriacetic acid (II) (pure for analysis) twice recrystallized from hot water were used for the syntheses.

Analysis. Carbon and hydrogen were determined by combustion in a single sample in a current of oxygen both without a catalyst and in the presence of chromic oxide. The metal was determined in the form of the oxide remaining after the calcination of the substance in a current of oxygen at 1000° C.

A description of the four methods of synthesis of I is given below.

1. An aqueous solution of a salt of the metal is added to a hot aqueous solution of an equimolecular amount of II. The solution is slowly evaporated to half its original volume. The crystals of I separating on cooling are filtered off with suction, washed with hot water, ethanol, and ether, and dried in vacuum.

2. A mixture of equimolecular amounts of the hydroxide (or oxide) of the metal and II is heated with an excess of boiling water for 3–4 hr. All the hydroxide (oxide) passes into solution, from which a precipitate of I deposits. It is filtered off with suction, washed with water, ethanol, and ether, and dried in vacuum. In the case of the synthesis of water-soluble hydrates, the clear solution of I obtained after the dissolution of the hydroxide (oxide) of the metal is filtered and evaporated. The crystals of I depositing are filtered off with suction and treated similarly.

3. Solutions of equimolecular amounts of the salt of the metal and II in anhydrous dimethylformamide are mixed. The precipitate that deposits is filtered off with suction, washed with dimethylformamide and ether, and dried in vacuum.

*For part XVIII, see [1].

Table 1

Metalloatrane-3,7,10-triones $\overbrace{N(CH_2COO)_3M}$ · nH_2O

M	n	Color of the crystals	Solubility[2*]	Empirical formula	Found, %					Calculated, %					Yield, % (method of preparation)
					C	H	N	metal	H_2O[5*]	C	H	N	metal	H_2O	
Nd^{III}	3	Pink	H_2O, $HCON(CH_3)_2$	$C_6H_{12}NO_9Nd$	18.97	3.72	3.31	37.00	14.20	18.63	3.13	3.63	37.34	13.97	75(4)
Ce^{III} [1*]	3	White	Insol.	$C_6H_{12}NO_9Ce$	19.46	2.82	3.07	36.60	10.00	18.90	2.90	3.67	36.76	9.44	62(1)
$HOPb^{IV}$ [1*]	2	White	H_2O(100°)	$C_6H_{11}NO_9Pb$	15.84	2.27	3.98	46.30	7.81	16.07	2.47	3.12	46.21	8.03	85(2)
$HOMn^{IV}$ [1*]	3	Gray	Insol.	$C_6H_{13}NO_{10}Mn$	23.66	4.14	4.74	18.49	18.00	22.94	4.17	4.45	17.49	17.31	65.5(2)
$ClTi^{IV}$ [1*]	2	White	$HCON(CH_3)_2$, $(CH_3)_2SO$	$C_6H_{10}NO_8TiCl$[3*]	22.53	3.52	4.43	14.98	12.20	23.43	3.27	4.55	15.50	11.71	72(3)
$ClZr^{IV}$[1*]	3	White	Insol.	$C_6H_{12}NO_9ZrCl$[4*]	19.61	3.87	3.99	23.61	15.10	19.53	3.27	3.79	24.73	14.65	67(1)
$HOOU^{VI}$	4	Yellow	$(CH_3)_2SO$, $HCON(CH_3)_2$	$C_6H_{15}NO_{12}U$	13.73	2.90	2.58	45.00	12.90	13.56	2.80	2.63	44.79	13.56	90(1)

[1*] New compound. [2*] The solvents in which the compound dissolves are given; insol. means that the substance is insoluble in all solvents. [3*] Found, %: Cl 11.38. Calculated, %: Cl 11.52. [4*] Found, %: Cl 9.65. Calculated, %: Cl 10.85. [5*] Content of water of hydration determined from the loss in weight on thermographic curves.

Table 2

$N(CH_2COO)_3M$ · $mN(CH_2COOH)_3$ · nH_2O

M	n	m	Color of crystals	Solubility**	Empirical formula	Found, %					Calculated, %					Yield, %
						C	H	N	metal	H_2O	C	H	N	metal	H_2O	
Nd^{III}*	6	1	Lilac	H_2O	$C_{12}H_{27}N_2O_{12}Nd$	22.36	4.51	4.92	22.40	19.60	22.82	4.30	4.43	22.84	20.17	81(2)
Th^{IV}	3.5	1	White	H_2O (100°)	$C_{12}H_{33}N_3O_{25}Th$	18.38	2.94	2.84	38.20	13.80	18.70	2.88	3.64	40.19	11.63	78(1)
Sb^{III}	0	4	White	H_2O; $HCON(CH_3)_2$ $(CH_3)_2SO$	$C_{30}H_{54}N_5O_{30}Sb$	33.43	4.14	6.81	11.60	0	33.52	3.94	6.52	11.34	—	77(2)
Sb^{III}*	1	3	White	H_2O, $HCON(CH_3)_2$ $(CH_3)_2SO$	$C_{24}H_{44}N_4O_{25}Sb$	30.12	4.94	5.99	13.81	2.3	31.66	4.87	6.15	13.37	1.97	70(2)
Co^{III}*	4	1	Pink	$(CH_3)_2SO$	$C_{12}H_{26}N_2O_{16}Co$	27.33	4.84	5.94	12.50	—	28.07	5.10	5.45	11.48	—	98,5(2)
Ni^{III}*	4	1	Blue	$(CH_3)_2SO$	$C_{12}H_{26}N_2O_{16}Ni$	28.38	4.58	5.14	11.0	14.10	28.09	5.10	5.46	11.44	14.03	56(2)

*New compound. ** The solvents in which the compound dissolves are given.

4. Aqueous solutions of equimolecular amounts of the metal salt and the trisodium salt of II are mixed. On standing a precipitate of I deposits, which is filtered off with suction, washed with hot water, ethanol, and ether, and dried in vacuum.

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