ATRANES

XVI. Metallo(III)atrane-3,7,10-triones*

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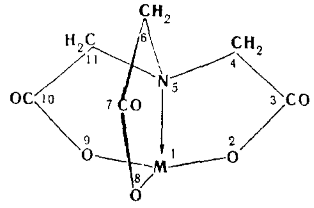
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 1, pp. 49–51, 1969

UDC 547.89'547.466'546.27.681.682.711.74

General methods for obtaining metallo(III)atrane-3,7,10-triones $N(CH_2COO)_3M^{III}$ (where M is an atom of a tervalent metal) and their hydrates are described. By means of these methods, a number of internally complexed compounds of this type have been synthesized, many of which (with M = B, Ga, In, Mn^{III}, Ni^{III}) were previously unknown.

Developing investigations in the field of the internally complexed metal derivatives of triethanolamine—the metalloatranes $N(CH_2CH_2O)_3M$, we have taken up the study of internally complexed salts of aminotriacetic acid $N(CH_2COOH)_3$ (I), generally incorrectly called nitrilotriacetic acid, which have an analogous structure and can be formally called metalloatrane-3, 7,10-triones (II):



In the formula of II, M represents an atom of a tervalent metal which may be coordinately bound to molecules of water, ammonia, and other ligands.

The study of the possibilities of the analytical use of complexed compounds of metal cations with I began more than 20 years ago. The considerable stability and simple composition of these complexes has permitted the use of titrated solutions of I in volumetric, gravimetric, polarographic, colorimetric, and other methods of analysis, and also as masking reagents [2–10]. However, the number of papers devoted to the study of the complexes II and their hydrates in the individual state and to the study of their properties is extremely limited, and they cover only a small number of metals. The majority of known metallic complexes II have been obtained in aqueous solutions and contain coordinately bound water.

Up to the present time, complexed compounds of aminotriacetic acid with the following metals have been isolated and described: Al [11,12], Sc [11], Y [11], La [13–17], Ce [18], Nd [13,14], Th [13], Sb [13], Bi [13,19,20], Cr [13], U [13,21], Fe [21] and Co [22].

In the present communication we describe five general methods for the synthesis of II and their hydrates in which M is an atom of a tervalent metal and previously unknown representatives of these compounds with M = B, Ga, In, Mn^{III}, and Ni^{III}.

The methods of preparation, the yields, the analytical data, the colors, and the solubilities of these compounds are given in the table. When they were prepared in aqueous solutions, all the II were obtained in the form of hydrates containing 1–3 molecules of H_2O. It was impossible to obtain II with M = B in aqueous solution. The majority of the $II \cdot nH_2O$ obtained can be dehydrated by heating in vacuum at 180–250° C.

In the future we propose a broad study of the physical and chemical properties, and also the physiological and catalytic activities of the metalloatrane-3,7,10-triones that are derivatives of tervalent and higher valency metals, and also a study of their complex compounds.

EXPERIMENTAL

Starting materials. The syntheses were carried out with chemically pure salts of tervalent metals with volatile acids (chlorides, acetates), or with freshly-prepared hydroxides of these metals, and with aminotriacetic acid (pure for analysis) recrystallized twice from hot water.

A description of the five methods of synthesis of II or their hydrates is given below.

1) An aqueous solution of the metal salt is added to a hot aqueous solution of an equimolar amount of aminotriacetic acid. After cooling, the water and the volatile acid formed are distilled off in a rotary vacuum evaporator with heating to 40° C. The dry residue is suspended in ethanol, filtered off with suction, washed with hot water (in the case of the II hydrates insoluble in H_2O) and with alcohol and ether and is dried in vacuum.

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

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

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*For part XV, see [1].

Metalloatrane-3,7,10-triones $N(CH_2COO)_3M^{III} \cdot nH_2O$

M	*n*	Color of the crystal	Solubility 2*	Empirical formula	Found, %					Calculated, %					Yield,% (method of preparation)
					C	H	N	M 3*	H_2O 4*	C	H	N	M	H_2O	
B	0	White	$HCON(CH_3)_2$	$C_6H_6NO_6B$1*	36.62	3.19	7.01	5.02	0.0	36.22	3.04	7.04	5.43	0.00	73.8 (4)
Al	2	White	H_2O, $HCON(CH_3)_2$ $(CH_3)_2SO$	$C_6H_{10}NO_8Al$	28.54	4.10	5.47	10.79	15.2	28.69	4.01	5.57	10.74	14.34	71.5 (3)
Al	0	Light brown	H_2O, $(CH_3)_2SO$	$C_6H_6NO_6Al$	33.72	2.63	6.60	13.01	0.0	33.50	2.81	6.51	12.54	0.00	91.5 (6)
Ga	2	White	H_2O, $(CH_3)_2SO$	$C_6H_{10}NO_8Ga$1*	24.62	3.29	5.00	24.10	12.31	24.52	3.42	4.76	23.72	12.26	79.5 (1)
Ga	1	Light beige	$(CH_3)_2SO$	$C_6H_6NO_6Ga$1*	26.00	2.89	4.87	27.60	6.80	26.10	2.92	5.07	25.29	6.56	91.8 (6)
In	2	White	H_2O, $(CH_3)_2SO$	$C_6H_{10}NO_8In$1*	21.39	3.02	4.31	33.60	12.1	21.25	2.97	4.13	33.87	10.62	81.6 (3)
La	3	White	Insol.	$C_6H_{12}NO_9La$	18.84	3.12	3.64	36.55	14.5	18.91	3.17	3.67	36.45	14.18	91.9 (1); 76.5 (5)
La	0	White	Insol.	$C_6H_6NO_6La$	22.20	2.00	4.23	43.08	0.0	22.03	1.84	4.28	42.47	0.00	90.4 (6)
Tl	2	White	H_2O	$C_6H_{10}NO_8Tl$1*	16.90	2.24	3.73	48.11	8.0	16.84	2.35	3.26	47.69	8.40	84.40 (3)
Bi	3	White	$(CH_3)_2SO$	$C_6H_{12}NO_9Bi$	16.47	2.67	3.23	47.25	13.8	16.33	2.28	3.17	47.37	12.24	81.3 (3)
Cr	3	Violet	H_2O, $HCON(CH_3)_2$ $(CH_3)_2SO$	$C_6H_{12}NO_9Cr$	24.27	4.68	4.41	17.38	17.9	24.49	4.11	4.76	17.67	18.37	99.0 (1); 87.7 (3)
Cr	1	Dark violet	Insol.	$C_6H_8NO_7Cr$	28.31	3.72	5.90	21.08	6.3	27.92	3.13	5.43	20.14	6.97	94.0 (6)
Mn	1	White	Insol.	$C_6H_8NO_7Mn$1*	27.86	3.00	4.94	21.00	6.66	27.60	3.08	5.36	21.04	6.9	61.1 (2); 53.2 (3)
Fe	1	Yellowish green	$(CH_3)_2SO$	$C_6H_8NO_7Fe$	27.10	3.25	5.62	20.51	8.0	27.51	3.08	5.35	21.32	6.87	80.0 (1); 76.8 (2); 73.0 (3); 61.5 (5)
Fe	0	Brown	Insol.	$C_6H_6NO_6Fe$	29.31	2.41	6.03	21.98	0.0	29.53	2.47	5.74	22.89	0.00	80.5(4); 92.3 (6)
Co	3	Pink	H_2O, $(CH_3)_2SO$	$C_6H_{12}NO_9Co$	23.91	4.31	4.82	20.00	17.5	23.93	4.01	4.65	19.57	17.95	77.1 (3)
Co	0	Dark pink	H_2O, $(CH_3)_2SO$	$C_6H_6NO_6Co$	32.12	2.85	6.32	26.12	0.0	31.73	2.66	6.16	25.95	0.00	90.8 (6)
Ni	3	Green	H_2O	$C_6H_{12}NO_9Ni$1*	24.03	4.13	4.78	19.85	15.23	23.95	3.99	4.65	19.51	17.96	60.2 (3)

1*New compound. 2*The solvent in which the compound is soluble is shown; insol.-substance insoluble in all common solvents. 3*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. 4*The content of water of hydration was determined from the loss in weight on the thermographic curves.

4) An equimolecular mixture of the metal and I is heated in boiling anhydrous dimethylformamide or dimethyl sulfoxide for 2–3 hr. The precipitate that deposits is filtered off with suction, washed with ethanol and ether, and dried in vacuum. The II obtained is purified by recrystallization from dimethylformamide

5) Hot solutions of equimolecular amounts of metal salt and the trisodium or tripotassium salt of I are mixed. The mixture is heated to the boil for 2–3 hr, filtered, evaporated, and slowly cooled to 0° C. The precipitate that deposits is filtered off with suction, washed with hot water, ethanol, and ether, and dried in vacuum.

6) The II • nH_2O obtained by the above methods (apart from method 4) are converted into the anhydrous II by heating in a vacuum of 1 mm at 160–220° C to constant weight.

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2 November 1966

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