

COORDINATION COMPOUNDS OF SOME SCANDIUM SALTS WITH 4-BUTYROLACTAM AND 8-CAPRYLOLACTAM

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Coordination compounds of scandium salts with 4-butyrolactam and 8-caprylolactam were prepared and their stoichiometric composition determined. The compounds prepared have been studied using TGA, DTA, X-ray method, and infrared spectroscopy. The conductivity measurements were made and molecular weights determined by cryoscopic method. All the compounds quoted were found to be anhydrous and lactams are in them coordinated through the oxygen atom of the C=O group.

A great attention has been recently given to the study of coordinated compounds in which lactams are present in terms of ligands. Complexes both with transition¹⁻³ and intranition⁴⁻⁶ elements were prepared. The coordination compounds with lactams are of interest not only from the theoretical point of view, but also because of the practical application in the purification process of lactams, or in terms of a modifying or catalyzing component in the polymerizations of lactams^{5,7}. Lactams with lower number of carbon atoms, primarily 4-butyrolactam^{1,3,6}, were mainly used as ligands. In all the cases studied, lactams behaved as single-bonded ligands, linked to a central atom by means of the oxygen atom of the C=O group. When preparing the complexes, the authors started either from anhydrous salts and benzene or ethyl alcohol solutions^{3,4} of lactam, or if the hydrates had to be employed, the latter were beforehand dehydrated with 2,2-dimethoxypropane^{2,8}. None of the papers quoted deals with complexes of scandium, and 8-caprylolactam as ligand was used only in the paper of Hart and Davis⁸.

EXPERIMENTAL

Reagents

In order to prepare coordination compounds, crystalline hydrated salts $\text{Sc}(\text{ClO}_4)_3 \cdot 7 \text{H}_2\text{O}$, $\text{Sc}(\text{NO}_3)_3 \cdot 4 \text{H}_2\text{O}$, $\text{ScCl}_3 \cdot 6 \text{H}_2\text{O}$, and $\text{ScBr}_3 \cdot 6 \text{H}_2\text{O}$ were used. The compounds were obtained by dissolution of scandium oxide (99.5%) in excess of relevant concentrated acids of the A.R. grade and by subsequent crystallization. The salts were analyzed for scandium and anion contents before use. Scandium thiocyanate was not prepared in terms of a solid, but its ether solution was made use of, obtained by extraction from a water solution of scandium trichloride and ammonium thiocyanate.

TABLE I
Results of Analyses of Coordination Compounds

Compound	% Sc		% C		% H	
	calc.	found	calc.	found	calc.	found
<i>I</i>	5.26	5.16	33.7	33.7	4.93	5.00
<i>II</i>	6.85	6.85	36.6	37.9	5.33	5.38
<i>III</i>	9.14	8.85	39.0	38.5	5.68	5.92
<i>IV</i>	5.65	5.60	36.4	35.1	5.28	5.47
<i>V</i>	8.05	8.06	40.7	40.0	5.04	5.04
<i>VI</i>	3.77	3.80	48.4	47.5	7.56	7.40
<i>VII</i>	4.80	4.92	51.2	51.2	8.06	8.05
<i>VIII</i>	6.28	6.20	53.6	54.2	8.38	8.28
<i>IX</i>	4.53	4.52	48.5	46.5	7.56	7.65
<i>X</i>	5.74	6.12	49.1	49.8	7.71	8.05

4-Butyrolactam, C_3H_6CONH , product of Fluka A.G., was redistilled and dried over a molecular sieve. 8-Caprylactam, $C_7H_{14}CONH$, product of BASF, was recrystallized from acetone, water, and benzene and dried at $50^\circ C$ under vacuum.

Preparation of Complexes

The coordination compounds of scandium perchlorate, nitrate, chloride, and bromide were prepared by dissolution of 0.01 mol of a scandium salt in 30 ml of triethylformate, and the solution was heated to $50^\circ C$ for approx. 15 minutes. To the solution, 0.06 mol of lactam dissolved in benzene was added. Crystalline compounds with 4-butyrolactam were obtained after evaporation of a part of the solvent under vacuum. The compounds with 8-caprylactam were precipitated from the solution by ether, washed, and dried in the same way as the coordination compounds with 4-butyrolactam. The thiocyanate complexes were produced by addition of the benzene solution of 0.06 mol of lactam to the ether solution containing 0.01 mol of scandium thiocyanate. The complex with 4-butyrolactam was separated directly, that with 8-caprylactam was separated very slowly after several hours standing.

Analytical

The scandium content was determined complexometrically⁹. The other elements were determined by elemental analysis. In addition, in complexes with 4-butyrolactam the anion content was established. The perchlorate and nitrate ions were determined by alkalimetry after dissolving the complex in water and passing it through the ion exchanger (Dowex 50) in the H^+ cycle. The chloride, bromide, and thiocyanate anions were determined by potentiometric titration of aqueous solution with silver nitrate.

TABLE I
(continued)

% N		% Other elements		% Anions	
calc.	found	calc.	found	calc.	found
9.84	9.74	12.5	13.2 ^a	35.0	35.2
17.08	16.86	—	—	28.3	29.0
11.37	11.09	21.6	21.6 ^a	21.6	20.9
10.55	9.65	30.1	30.8 ^b	30.1	29.9
17.52	17.54	17.25	17.23 ^c	31.1	32.0
7.06	6.84	9.75	10.03 ^a	—	—
11.95	11.45	—	—	—	—
7.81	7.83	14.65	14.86 ^a	—	—
7.06	6.97	24.2	25.1 ^b	—	—
12.25	11.96	12.37	13.5 ^c	—	—

^a Chlorine, ^b bromine, ^c sulphur.

Physico-Chemical Measurements

The infrared spectra were measured in KBr pellets with use of spectrograph Perkin-Elmer 325, over a range of 200–4000 cm^{-1} . The X-ray measurements involving the Debye–Scherrer method were carried out on diffractograph Geigerflex (Rigaku-Denki, Japan), CoK_{α} , Fe filter in a region of 2 to 30°. The melting points were established on a heated microscope stage Boetius (Küstner). The molecular weight was determined by conventional cryoscopic method in nitrobenzene. The conductivity measurements of 0.001M water, N,N-dimethylformamide, and nitrobenzene solutions at 25°C were made using the RLC bridge Tesla BM 401 E (Tesla).

Behaviour of the substances during heating was followed by TGA, DTA, and by using apparatus described in previous papers¹⁰. The temperature increase was linear and amounted to 7°C/min.

RESULTS AND DISCUSSION

As follows from analytical results (Table I) the complex compounds of the following composition were obtained in the reaction of scandium hydrate salts with 4-butyrolactam and 8-caprylolactam under given conditions: $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_6](\text{ClO}_4)_3$ (I), $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_5(\text{NO}_3)](\text{NO}_3)_2$ (II), $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_4\text{Cl}_2]\text{Cl}$ (III), $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_6]\text{Br}_3$ (IV), $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_4(\text{SCN})_2]\text{SCN}$ (V), $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_6](\text{ClO}_4)_3$ (VI), $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_5(\text{NO}_3)](\text{NO}_3)_2$ (VII), $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_4\text{Cl}_2]\text{Cl}$ (VIII), $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_5\text{Br}]\text{Br}_2$ (IX), $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_4(\text{SCN})_2]\text{SCN}$ (X).

The Debye–Scherrer method shows that all the compounds prepared are crystalline substances of low symmetry.

TABLE II
Characteristic Vibration of the C=O Group in Infrared Spectra

Compound	$\nu_{\text{C}=\text{O}}, \text{cm}^{-1}$		$\Delta\nu_{\text{C}=\text{O}}, \text{cm}^{-1}$
	free lactam	coordinated lactam	
<i>I</i>	1 682	1 640	-42
<i>II</i>	1 682	1 635	-47
<i>III</i>	1 682	1 635	-47
<i>IV</i>	1 682	1 635	-47
<i>V</i>	1 682	1 640	-42
<i>VI</i>	1 654	1 615	-39
<i>VII</i>	1 654	1 615	-39
<i>VIII</i>	1 654	1 610	-44
<i>IX</i>	1 654	1 610	-44
<i>X</i>	1 654	1 610	-44

TABLE III
Conductivity Measurement and Determination of Molecular Weight

Compound	$\Lambda, \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$			Molecular weight		Number of particles in the solution
	water	dimethyl-formamide	nitrobenzene	calc.	found	
<i>I</i>	412	203	69.4	854	225	4
<i>II</i>	400	128	1.1	657	156	4
<i>III</i>	406	69	—	—	—	—
<i>IV</i>	440	163	—	—	—	—
<i>V</i>	425	137	—	—	—	—
<i>VI</i>	450	222	69.6	1 191	286	4
<i>VII</i>	408	163	0.6	937	250	4
<i>VIII</i>	400	78	—	—	—	—
<i>IX</i>	433	162	—	—	—	—
<i>X</i>	395	155	—	—	—	—

In the infrared spectra of the compounds achieved, frequencies corresponding to vibrations of the C=O group of lactams (Table II) were primarily examined. A characteristic shift of the frequency towards a lower value in the bound lactam points, in comparison with free lactam, to the coordination of the ligand by means

TABLE IV
Results of Thermal Analysis

Compound	Weight loss ^a		Melting point ^b °C	Onset of decomposition
	calc.	found		
<i>I</i>	9.19	— ^c	182	200
<i>II</i>	89.5	— ^c	77	140
<i>III</i>	86.0	85.0	185	180
<i>IV</i>	91.3	90.6	105	120
<i>V</i>	87.7	87.6	147	140
<i>VI</i>	94.2	— ^c	170	220
<i>VII</i>	92.6	— ^c	135	150
<i>VIII</i>	90.4	89.6	209	200
<i>IX</i>	93.0	92.4	124	180
<i>X</i>	91.2	88.6	115	180

^a Corresponds to the formation of Sc_2O_3 , ^b with a precision of $\pm 2^\circ\text{C}$, ^c in the explosive course of the decomposition, the loss of weight was not measurable.

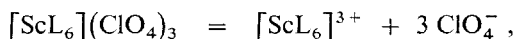
of the electron pair of the oxygen atom coming from the $\text{C}=\text{O}$ group and, as a result of this, to the decrease of the order of bond in this group. The magnitude of this shift is $40\text{--}50\text{ cm}^{-1}$ and consequently, a conclusion may be drawn as to the formation of a relatively strong bond between ligand and central Sc^{3+} ion. In the nitrate complexes spectra (*II* and *VII*) an intense absorption band at 1380 cm^{-1} was found, which corresponds to a ν_3 vibration of the ionic bonded NO_3^- group of D_{3h} symmetry, and a relatively intense absorption band at 1300 cm^{-1} as well as a band of lower intensity at 750 cm^{-1} , which correspond to the ν_1 and ν_3 vibrations of the coordinately bonded NO_3^- group of symmetry¹¹ C_{2v} .

The compounds *II* and *VII* may be assumed to have their NO_3^- ions either coordinated in the inner coordination sphere and likewise bonded as anion in the outer sphere. The coordination number of the scandium ion is completed to six by the NO_3^- ligand. Analogously, completion of the coordination number of the scandium ion by the coordinated anion may be assumed also with other compounds for which less than six molecules of lactam were found. It was not possible to find a direct proof for this assumption from the infrared spectra.

The results of conductivity and cryoscopic measurements are summarized in Table III. In an aqueous solution, all the prepared substances dissociate as 1 : 3 electrolytes and owing to a great affinity of the scandium ion to water, a complete decomposition of the complex can be assumed. Likewise analytical determinations of anions (Table I) confirm that none of the anions is bonded in the aqueous solution in the inner complex sphere. In *N,N*-dimethylformamide the perchlorate complexes only

(*I* and *VI*) dissociate as 1 : 3 electrolyte, whereas the nitrate, bromide, and thiocyanate complexes (*II*, *IV*, *V*, *VIII*, and *X*) dissociate as 1 : 2 electrolytes and the chlorine complexes (*III* and *VIII*) as 1 : 1 electrolytes¹². This dissociation is in most cases in accordance with the assumed type of the anion bond in crystalline coordination compound.

In the least polar solvent, nitrobenzene, the measurement was largely limited by a very low solubility of the substances examined so that the conductivity and cryoscopic measurements could be made with perchlorate and nitrate complexes only. Compounds *I* and *VI* dissociate in nitrobenzene as 1 : 3 electrolytes and in view of the fact that molecular weights, determined cryoscopically, point to the decomposition into 4 particles, a conclusion may be made that dissolution of the substances quoted takes place in nitrobenzene under a simultaneous dissociation according to equation



where L = lactam. The nitrate complexes behave in nitrobenzene as nonelectrolytes, but the cryoscopic determination of the molecular weight suggests a decomposition into 4 particles. Dissociation of these complexes in nitrobenzene can be then expressed by

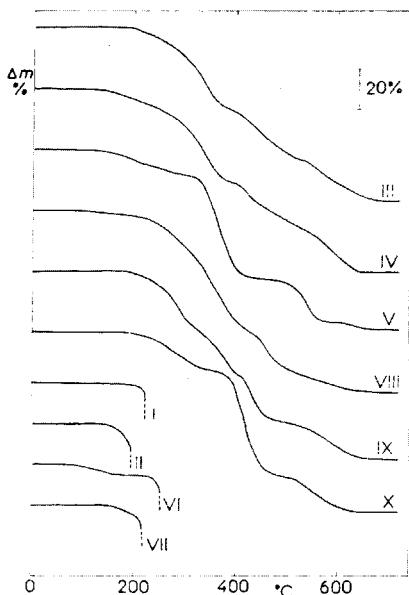


FIG. 1

TGA Curves of Coordination Compounds
 I $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_6](\text{ClO}_4)_3$, II $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_5(\text{NO}_3)](\text{NO}_3)_2$, III $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_4\text{Cl}_2]\text{Cl}$, IV $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_6]\text{Br}_3$, V $[\text{Sc}(\text{C}_3\text{H}_6\text{CONH})_4(\text{SCN})_2]\text{SCN}$, VI $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_6](\text{ClO}_4)_3$, VII $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_5(\text{NO}_3)](\text{NO}_3)_2$, VIII $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_4\text{Cl}_2]\text{Cl}$, IX $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_5\text{Br}]\text{Br}_2$, and X $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_4(\text{SCN})_2]\text{SCN}$. (Δm = loss of weight).

The coordination number of the scandium ion can be then in this case completed to six either by coordination of the solvent molecule³, or by a double-bonded nitrate ligand.

With respect to the possible utilization in the polymerizations of lactams, it was of interest to examine behaviour of the prepared substances during heating. The course of thermal decomposition shows (Fig. 1) that the compounds investigated may be divided into two groups. The first group comprises salts which have an anion with oxidation effects—perchlorates (*I* and *VI*) and nitrates (*II* and *VII*). These compounds decompose virtually at once and with explosion at temperatures about 200°C (Table IV). The most stable of them is the perchlorate complex with 8-caprylolactam (*VI*), which is stable approx. up to 220°C.

The second group includes complexes whose anion has no oxidation effects, *i.e.* chloride (*III* and *VIII*), bromide (*IV* and *IX*), and thiocyanate (*V* and *X*) complexes. In these compounds a stepwise decomposition takes place and the thermogravimetric curves (Fig. 1) show delays which point to the course of decomposition in several stages. Weight losses correspond in some cases to the formation of complexes of a lower coordination number (for instance, loss of weight of $[\text{Sc}(\text{C}_7\text{H}_{14}\text{CONH})_4 \cdot (\text{SCN})_2]\text{SCN}$, amounting to 18% at 350°C, corresponds to the value calculated for the loss of one molecule of lactam), but formation of defined intermediate products has not been proved.

At higher temperature, all the compounds decompose to form Sc_2O_3 . The weight loss found is in agreement with the calculated value.

Differential thermal analysis made it possible to find a strong exothermic effect within a temperature range of 500 to 600°C, when combustion of the rests of an organic ligand by means of air oxygen takes place. The explosive decomposition of the first group of complexes manifests itself likewise by a strong exothermic effect. Thermal effects during heating of complexes of the second group, except for the endothermic effect in the course of melting, are not too distinct.

The difference in size of the lactam ring (5-membered and 9-membered rings for 4-butyrolactam and 8-caprylolactam, respectively), has no effect, except for bromide complexes, on the composition of the complexes; likewise the shift of frequency of the C=O bond during formation of the complexes is practically equal, only from the viewpoint of thermal stability, the complexes with 8-caprylolactam appear as somewhat more stable ones.

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