

THE CRYSTAL AND MOLECULAR STRUCTURE
OF TRIS(1-AZA-2-CYCLONONANONE-O)-
-TRICHLOROCHROMIUM(III) COMPLEX

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The title compound crystallizes in the monoclinic system, has the $P2_1/c$ space group, and the unit cell parameters are $a = 1484.4(8)$, $b = 1522.8(8)$, $c = 1854.0(8)$ pm, $\beta = 96.36(4)^\circ$, $Z = 4$. The structure consists of molecules of an electroneutral complex interconnected only through the van der Waals forces. Solvent is nonstoichiometrically incorporated in the crystals. Octanolactam monodentate ligands are coordinated through oxygen atoms to Cr(III) and have the *cis*-conformation of the amide group. The relationship between structure parameters of the amide group, their change caused by coordination and the reactivity of the amide group to nucleophilic substitution are discussed using the example of octanolactam polymerization.

Transition and nontransition metal complexes of lactams have been extensively studied^{1,2}. They are used for analytical^{3,4} and technical purposes as initiators of the polymerization of lactams⁵ or epoxy resins⁶, or as modifiers of the properties of polyamides⁷. Knowledge of the structure of lactam complexes is very important for the study of the coordination behaviour of the amide group. Using an amide cycle or polycycle of different sizes, it is possible to fix the planar or nonplanar, *cis* or *trans* conformations of the amide group⁸⁻¹⁰. Since the size of the cycle (from pyrrolidone to dodecanolactam) has no influence on the coordination number of the central atom¹¹, the possibility of generalization of the results can be assumed.

Spectroscopy has been so far most in use for the characterization of lactam coordination compounds. However, the basic question whether the amide O or N is the coordinating atom often cannot be answered unambiguously using the spectra. As a result, several contradictory mechanisms^{12,13} have been suggested for some reactions of amides, even for those frequently examined. No molecular structure of any coordination compound of lactams has been published so far. It can be expected that results of X-ray structure analysis will play an important role in the solution of these problems.

EXPERIMENTAL

Preparation of Single Crystals

The title complex crystallized from a toluene solution containing 0.02 mol $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ and 0.06 mol 1-aza-2-cyclononane (octanolactam) after azeotropic dehydration and cooling. The crystals were grown by slow cooling of the solution in dry benzene, washed with ether and dried in vacuo. Since they are slightly hygroscopic, all operations were performed in nitrogen atmosphere, and the crystal was sealed in a glass capillary for diffraction measurements.

The density $D_0 = 1.185 \text{ Mg m}^{-3}$ was determined pycnometrically in n-heptane, the melting point was determined microscopically (121–124°C). The mass spectroscopic method and $^1\text{H-NMR}$ revealed that the crystals contained a solvent, benzene and toluene molecules, and also tetrachloroethane if the latter was used in the crystallization. The content of the aromatic solvent in crystals varied from 0.5 to 1.5 mol per mol of complex for various preparations. It never drops below 0.5 mol even after storage in a desiccator for several years. Analysis: for $(\text{C}_8\text{H}_{15} \cdot \text{ON})_3 \cdot (\text{C}_7\text{H}_8)_{0.8} \cdot (\text{C}_6\text{H}_6)_{0.7} \cdot \text{CrCl}_3$ (710.4) calculated: 57.14% C, 7.89% H, 5.91% N; for measured crystals found: 57.13% C, 8.02% H, 5.78% N.

Crystallographic Data

The lattice parameters $a = 1484.4(8)$, $b = 1522.8(8)$, $c = 1854.0(8)$ pm, $\beta = 96.36(4)^\circ$ were refined by the least squares method from 15 reflexions measured with a Syntex $P2_1$ diffractometer. The experimentally determined crystal density $D_0 = 1.185(5) \text{ Mg m}^{-3}$ is in good agreement with $D_x = 1.181(2) \text{ Mg m}^{-3}$ calculated from the unit cell parameters given above and from the molecular formula determined from elemental analysis. Systematic extinctions checked by film methods indicated the $P2_1/c$ crystallographic space group. From 3968 symmetrically independent reflexions measured on a Syntex $P2_1$ automatic diffractometer, 818 were classified as unobserved using criterion $I < 1.96\sigma(I)$.

The absorption, Lorentz and polarization corrections were applied.

Structure Determination and Refinement

The positions of chromium and chlorine atoms were calculated with MULTAN 74 program¹⁴. The combined Fourier and LS methods showed all the remaining nonhydrogen atoms. The structure was refined by using a modified least squares NRC 10 program¹⁵. Hydrogen atoms belonging to not well localized carbon atoms (from C(33) to C(37) and atoms of the solvent molecules) were excluded from the least squares refinement. All the remaining hydrogen atoms were fixed in calculated optimal positions. The function minimized was $\sum w\Delta^2$ where $w = [\sigma_F^2 + (0.03F_0)^2]^{-1}$ and $\Delta = ||F_o| - |F_c||$. The atomic scattering factors were taken from the literature¹⁶; the hydrogen atoms were considered to be a spherical approximation of bound atoms. Unobserved reflexions were not used in the analysis.

Nonhydrogen atoms were refined with anisotropic temperature factors until all parameter shifts were lower than 0.5 of the corresponding estimated standard deviations. The final agreement factors are

$$R_1 = \sum \Delta / \sum |F_o| = 0.092, R_2 = [\sum \Delta^2 / \sum |F_o|^2]^{1/2} = 0.114,$$

$$R_{w2} = [\sum w\Delta^2 / \sum w|F_o|^2]^{1/2} = 0.112, S = [\sum w\Delta^2 / (m - n)]^{1/2} = 1.05,$$

where m is the number of reflexions used in the refinement (3150) and n is the number of refined

parameters (564). The resulting position parameters and B_{eq} (ref.¹⁷) of nonhydrogen atoms are summarized in Table I. The corresponding anisotropic temperature factors are tabulated in Table II. The final difference map did not possess any important features.

RESULTS AND DISCUSSION

The complex is composed of three lactam molecules bound through an oxygen atom on Cr(III) and through bifurcated hydrogen bonds $N-H \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$ on chlorine atoms (Figs 1–4). Three oxygen and three chlorine atoms thus form a tetragonal bipyramidal arrangement around the central Cr atom; the mean distance of the oxy-

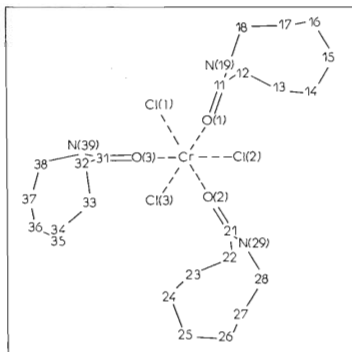


FIG. 1

Numbering scheme. Projection along the normal of the plane Cl(1), Cl(2), Cl(3)

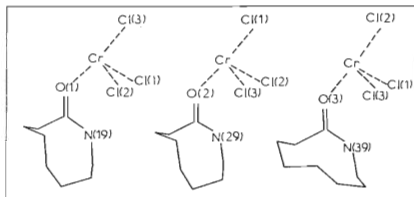


FIG. 2

Conformation of ligands. The projection plane is formed by O—C—N atoms

TABLE I

Final positional parameters, their estimated standard deviations ($\times 10^4$) and B_{eq} values ($\times 10^{-4}$ pm²) of the non-H atoms

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	B_{eq}
Cr	3 235(1)	5 452(1)	6 642(1)	4.0
Cl(1)	4 877(1)	5 608(1)	6 742(1)	4.9
Cl(2)	2 997(1)	6 938(1)	6 393(1)	5.2
Cl(3)	3 244(1)	5 618(1)	7 889(1)	5.3
Ligand (1)				
O(1)	3 127(3)	5 189(3)	5 580 (3)	4.9
C(11)	3 526(6)	5 460(5)	5 023(4)	4.8
C(12)	3 162(6)	5 095(6)	4 309(4)	5.6
C(13)	2 210(7)	5 505(7)	4 020(6)	7.6
C(14)	2 165(7)	6 525(8)	4 052(6)	8.7
C(15)	2 592(8)	6 990(8)	3 463(6)	9.4
C(16)	3 638(8)	6 917(7)	3 399(6)	8.6
C(17)	4 277(7)	7 182(7)	4 093(6)	7.6
C(18)	4 730(6)	6 415(6)	4 526(5)	6.0
N(19)	4 187(5)	6 064(4)	5 095(3)	5.3
Ligand (2)				
O(2)	1 845(3)	5 215(3)	6 545(3)	4.8
C(21)	1 131(5)	5 574(5)	6 785(5)	5.2
C(22)	244(6)	5 038(6)	6 721(5)	6.6
C(23)	327(7)	4 296(7)	7 260(7)	8.5
C(24)	694(8)	4 560(7)	8 043(7)	9.6
C(25)	— 19(9)	5 000(9)	8 489(8)	11.8
C(26)	— 467(8)	5 854(8)	8 211(6)	9.5
C(27)	232(7)	6 614(7)	8 152(6)	8.3
C(28)	410(6)	6 831(6)	7 392(6)	7.7
N(29)	1 182(4)	6 323(4)	7 103(4)	5.6
Ligand (3)				
O(3)	3 341(3)	4 143(3)	6 720(3)	4.8
C(31)	3 777(5)	3 576(5)	7 132(5)	4.8
C(32)	3 500(7)	2 638(6)	6 999(6)	7.4
C(33)	2 525(8)	2 431(8)	7 237(7)	10.7
C(34)	2 542(13)	2 114(13)	8 044(10)	17.5
C(35)	2 875(11)	2 913(19)	8 570(8)	21.9
C(36)	3 641(13)	2 840(18)	8 931(9)	20.9
C(37)	4 532(10)	3 312(9)	8 939(6)	10.5
C(38)	4 897(7)	3 226(6)	8 219(6)	7.9
N(39)	4 437(5)	3 792(4)	7 644(4)	5.7

TABLE I
(Continued)

Atoms	x/a	y/b	z/c	B_{eq}
Toluene				
C(41)	3 303(12)	5 202(12)	1 638(8)	15·0
C(42)	2 682(10)	5 537(11)	1 188(8)	13·2
C(43)	2 791(9)	5 542(10)	462(8)	12·6
C(44)	3 499(11)	5 040(10)	180(10)	14·4
C(45)	4 088(12)	4 563(10)	632(8)	13·2
C(46)	4 023(11)	4 534(9)	1 324(8)	12·5
C(47)	2 253(16)	6 032(17)	-21(14)	23·0
Benzene				
C(51)	8 334(13)	7 842(20)	-298(7)	23·0
C(52)	8 913(12)	8 567(11)	-198(7)	15·1
C(53)	9 827(13)	8 511(11)	80(8)	14·0
C(54)	10 213(11)	7 754(12)	295(7)	14·3
C(55)	9 617(15)	7 037(8)	210(8)	16·3
C(56)	8 755(16)	7 089(16)	-63(9)	21·8

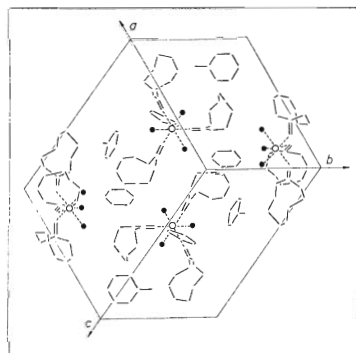


FIG. 3
Perspective view of the crystal structure.
The same projection as in Fig. 1

TABLE II

The anisotropic thermal coefficients ($\times 10^4$) in the expression $\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$ for all non-H atoms (estimated standard deviations are in brackets)

Atom	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Cr	45(1)	33(1)	38(1)	0(1)	24(1)	— 1(1)
Cl(1)	47(1)	49(1)	45(1)	3 (2)	23(1)	— 8(2)
Cl(2)	59(1)	35(1)	56(1)	6(2)	25(2)	— 5(2)
Cl(3)	67(1)	55(1)	39(1)	— 7(2)	30(2)	16(2)
Ligand (1)						
O(1)	59(3)	43(3)	43(2)	— 10(4)	21(4)	0(5)
C(11)	66(5)	35(4)	40(3)	— 4(6)	26(7)	6(7)
C(12)	70(6)	60(5)	39(3)	— 6(7)	31(7)	— 4(9)
C(13)	73(6)	91(7)	59(4)	26(9)	1(8)	— 36(11)
C(14)	80(7)	107(8)	70(5)	32(10)	47(9)	62(13)
C(15)	107(9)	92(8)	82(6)	62(11)	78(11)	32(13)
C(16)	120(9)	82(7)	61(5)	46(9)	66(10)	39(13)
C(17)	92(7)	71(6)	64(5)	23(8)	48(9)	— 36(11)
C(18)	66(6)	68(6)	47(4)	9(7)	39(7)	— 19(9)
N(19)	71(5)	56(4)	34(2)	— 1(5)	20(5)	— 26(7)
Ligand (2)						
O(2)	47(3)	40(3)	51(2)	— 13(4)	28(4)	— 1(5)
C(21)	47(5)	55(5)	49(3)	— 4(7)	13(6)	— 3(8)
C(22)	49(5)	71(6)	66(5)	— 34(8)	32(8)	— 13(9)
C(23)	69(7)	58(6)	107(7)	11(10)	53(10)	— 20(10)
C(24)	95(8)	86(8)	97(7)	85(11)	70(11)	63(12)
C(25)	132(11)	109(10)	111(8)	92(14)	132(15)	59(17)
C(26)	97(8)	103(8)	85(6)	18(11)	102(11)	54(13)
C(27)	101(8)	80(7)	68(5)	— 19(9)	68(10)	13(12)
C(28)	67(6)	56(6)	91(6)	— 7(9)	47(9)	31(9)
N(29)	53(4)	40(4)	64(3)	— 1(6)	35(6)	11(6)
Ligand (3)						
O(3)	58(3)	34(3)	47(2)	4(4)	25(4)	— 1(5)
C(31)	48(5)	37(4)	54(4)	11(6)	43(7)	11(7)
C(32)	79(7)	39(5)	84(5)	8(8)	4(9)	— 15(9)
C(33)	98(9)	95(8)	105(7)	90(13)	— 13(12)	— 79(14)
C(34)	193(16)	213(17)	109(9)	94(20)	— 61(19)	— 291(29)
C(35)	148(14)	476(36)	71(7)	68(25)	108(16)	278(36)
C(36)	176(16)	418(32)	72(7)	104(25)	120(17)	101(36)
C(37)	172(12)	113(9)	49(5)	29(10)	64(12)	14(17)
C(38)	103(8)	45(5)	78(5)	37(8)	7(10)	51(10)
N(39)	70(5)	40(4)	55(3)	16(5)	23(6)	4(7)

TABLE II
(Continued)

Atom	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Toluene						
C(41)	212(18)	147(13)	92(8)	27(15)	- 1(18)	- 207(25)
C(42)	136(12)	167(14)	94(8)	- 20(15)	55(15)	- 149(20)
C(43)	112(10)	134(12)	105(8)	61(15)	- 78(14)	- 35(16)
C(44)	174(15)	99(10)	141(11)	- 17(17)	62(19)	10(20)
C(45)	200(16)	112(11)	87(8)	18(14)	26(16)	39(20)
C(46)	206(16)	95(9)	81(7)	- 18(12)	54(16)	- 104(19)
C(47)	202(23)	236(25)	207(20)	- 48(35)	- 58(31)	- 9(36)
Benzene						
C(51)	197(18)	503(37)	44(6)	8(23)	84(15)	25(39)
C(52)	238(16)	192(14)	60(6)	75(14)	127(15)	274(26)
C(53)	249(18)	131(11)	70(6)	5(14)	135(16)	5(23)
C(54)	159(14)	240(18)	54(5)	29(16)	55(13)	92(24)
C(55)	359(24)	77(8)	92(8)	75(13)	218(22)	124(23)
C(56)	285(24)	344(28)	77(8)	- 120(25)	185(22)	- 247(42)

gen atoms from the chlorine atom is 202.9 pm and the mean distance of the chlorine atoms from the chromium atom is 236.3 pm. No intercomplex distances shorter than the van der Waals contacts were found.

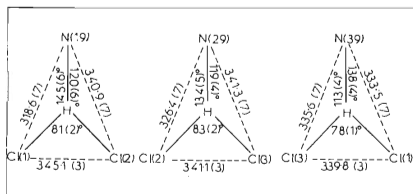


FIG. 4

Bifurcated hydrogen bonds between ligands of the complex

The numbering scheme of the atoms is shown in Fig. 1. Some interesting distances and angles around the central chromium atom are shown in Table III. Similar data on ligands are given in Tables IV and V. The torsion angles are given in Table VI.

TABLE III

Some interatomic distances (pm) and angles ($^{\circ}$) around the Cr atom (estimated standard deviations are in brackets)

Cr—Cl(1)	243.6(2)	Cl(1)—Cl(2)	345.1(3)
Cr—Cl(2)	232.8(2)	Cl(1)—Cl(3)	339.8(3)
Cr—Cl(3)	232.4(2)	Cl(2)—Cl(3)	341.1(3)
Cr—O(1)	200.0(5)	O(1)—O(2)	275.3(7)
Cr—O(2)	208.3(5)	O(1)—O(3)	263.8(7)
Cr—O(3)	200.4(5)	O(2)—O(3)	274.5(7)
Cl(1)—Cr—Cl(2)	92.8(1)	O(1)—O(2)—O(3)	57.3(2)
Cl(1)—Cr—Cl(3)	91.3(1)	O(1)—O(3)—O(2)	61.5(2)
Cl(2)—Cr—Cl(3)	94.3(1)	O(2)—O(1)—O(3)	61.2(2)
O(1)—Cr—O(2)	84.8(2)	Cl(1)—Cl(2)—Cl(3)	59.4(1)
O(1)—Cr—O(3)	82.4(2)	Cl(1)—Cl(3)—Cl(2)	60.9(1)
O(2)—Cr—O(3)	84.4(2)	Cl(2)—Cl(1)—Cl(3)	59.7(1)

TABLE IV

Some interatomic distances (pm) in the octanelactam ligands. Estimated standard deviations are in brackets

Atom	Ligand(1), $i = 1$	Ligand(2), $i = 2$	Ligand(3), $i = 3$
C(i1)—N(i9)	134(1)	128(1)	133(1)
C(i1)—O(i)	131(1)	131(1)	128(1)
C(i1)—C(i2)	148(1)	154(1)	150(1)
C(i2)—C(i3)	158(1)	150(1)	159(2)
C(i3)—C(i4)	156(2)	155(2)	157(2)
C(i4)—C(i5)	150(2)	157(2)	160(3)
C(i5)—C(i6)	157(2)	152(2)	130(3) ^a
C(i6)—C(i7)	156(2)	157(2)	150(3)
C(i7)—C(i8)	153(1)	150(1)	150(2)
C(i8)—N(i9)	150(1)	153(1)	148(1)

^a Uncertain atomic positions.

The geometry of the ligands is also depicted in Fig. 2. The following Fig. 3 shows the projection of the crystal structure perpendicularly to the plane Cl(1), Cl(2), Cl(3).

The nonstoichiometric incorporation of solvent molecules into the crystal is

TABLE V

Valence angles ($^{\circ}$) in the octanelactam ligands. Estimated standard deviations are in brackets

Angle	Ligand(1), $i = 1$	Ligand(2), $i = 2$	Ligand(3), $i = 3$
C(i1)—C(i2)—C(i3)	112.2(7)	110.0(8)	112.7(8)
C(i2)—C(i3)—C(i4)	114.8(8)	115.0(9)	114.0(11)
C(i3)—C(i4)—C(i5)	114.9(9)	114.7(10)	108.5(14)
C(i4)—C(i5)—C(i6)	121.4(10)	118.9(11)	117.1(22)
C(i5)—C(i6)—C(i7)	115.7(9)	112.7(10)	134.8(21) ^a
C(i6)—C(i7)—C(i8)	115.2(8)	114.6(9)	110.7(11)
C(i7)—C(i8)—N(i9)	113.8(7)	115.8(8)	114.0(9)
C(i8)—N(i9)—C(i1)	128.3(7)	127.1(7)	128.1(7)
N(i9)—C(i1)—C(i2)	122.5(7)	120.9(7)	121.4(7)
O(i)—C(i1)—N(i9)	121.8(7)	121.1(7)	123.0(7)
O(i)—C(i1)—C(i2)	115.6(7)	117.9(7)	115.6(7)

^a Uncertain atomic positions.

TABLE VI

Selected torsion angles ($^{\circ}$). Estimated standard deviations are approximately 2°

Angles	Ligand(1), $i = 1$	Ligand(2), $i = 2$	Ligand(3), $i = 3$
O(i)—C(i1)—C(i2)—C(i3)	73.4	72.0	— 70.2
O(i)—C(i1)—N(i9)—C(i8)	177.5	178.3	170.3
C(i1)—C(i2)—C(i3)—C(i4)	48.7	48.7	— 90.3
C(i2)—C(i3)—C(i4)—C(i5)	77.5	79.0	66.9
C(i3)—C(i4)—C(i5)—C(i6)	— 64.0	— 60.4	— 111.4
C(i4)—C(i5)—C(i6)—C(i7)	— 55.5	— 60.4	114.2
C(i5)—C(i6)—C(i7)—C(i8)	104.9	105.8	— 61.1
C(i6)—C(i7)—C(i8)—N(i9)	— 89.4	— 89.9	75.9
C(i7)—C(i8)—N(i9)—C(i1)	85.8	87.3	— 97.6
C(i8)—N(i9)—C(i1)—C(i2)	— 6.2	— 6.0	— 10.1
N(i9)—C(i1)—C(i2)—C(i3)	— 103.1	— 103.8	110.2
Cr—O(i)—C(i1)—N(i9)	0.1	10.3	— 8.5

obviously the cause underlying difficulties in the determination of their exact atomic parameters. This is the reason why the molecular parameters of solvents are not discussed in greater detail.

CrCl₃ Group

Lactam molecules produce only a weak ligand field, and no great effect on the structure parameters of CrCl₃ can therefore be expected. This is also confirmed by the Cr-Cl bond lengths in the complex (Table III) which can be compared¹⁸ with those in the CrCl₃ ionic crystal (234.0–234.7 pm), but are longer¹⁹ than in the [Cr(H₂O)₄.Cl₂]⁺ cation (228.9 pm).

Ligands

In solutions, octanolactam exists as two *cis* and two *trans* conformers⁹ differing in their energy^{20,21} only by 2–3 kJ mol⁻¹. Only a *transoid*, considerably non-planar arrangement of the amide group has been detected in its crystals²². In the crystals of the title complex, all three octanolactam molecules have the *cis* conformation and are coordinated through the oxygen atom. A similarly coordinated *cis* lactam has been observed in the case of crystalline octanolactam hydrochloride²³ and in solutions of the bis(1-methyl-1-aza-2-cyclononanone-O)-tetrachlorotitanium (IV) complex²⁴.

The conformations of the cycle of coordinated and noncoordinated octanolactam are in a good agreement with the *cis* and *trans* conformations of both cyclononane²⁵ and cyclononene²⁶, respectively. Differences between the valency angles of ligands (1) and (2) in the chromium(III) complex, octanolactam hydrochloride and *cis* cyclononene do not exceed 2°. Therefore the conformation of the nine-membered cycle does not seem to be affected by the coordination of the ligand to the central atom.

The low ordering of ligand (3) in the complex may be due to the presence of both possible *cis* conformations, because also in nonanolactam the strongly disordered crystal structure (*R* = 0.49)²⁷ is assigned to the existence of six *trans* conformers²⁸ with energy differences up to 10 kJ mol⁻¹.

Amide Group

Coordination of the lactams to CrCl₃ deeply changes the structure parameters of the amide group, probably as a consequence of a change in the π and simultaneously in the σ electron system, as has been demonstrated by the quantum chemical calculations *e.g.* for the protonation of model amides²⁹.

The reactivities of amides in acid catalyzed reactions are affected by the magnitude of polarization of the amide group. Its molecular parameters, such as the C(1)–O, C(1)–N bond lengths and the N–C(1)–O angle vary monotonically with the extent of the

O-coordination which increases starting from amides in the gas state through amides bound by hydrogen bonds in the condensed phase, and partly O-protonated amides, up to fully O-protonated amides³⁰. The most marked increase is observed with the length of the C-O bond; this length is comparable for the chromium(III) complex of octanolactam and octanolactam hydrochloride²³. The effect of O-coordination predominates over differences between the *cis-trans* conformations and nonplanar deformations of the amide group imposed by the cyclic structure of various lactams. The charge distribution of the amide group calculated by the CNDO/2 method for *cis* and *trans* N-methylacetamide and *cis* butanolactam is almost the same²⁹: C +0.36; N -0.20; O -0.35, but it varies greatly with O-protonation, as shown by the values C +0.47; N -0.10; O -0.17 for O-protonated *cis* and *trans* N-methylacetamide²⁹.

The charge distribution on the amide group of the lactam has as a consequence that the carbon atom of the carbonyl group of one molecule acts as an electron acceptor and the nitrogen atom of the other molecule acts as a donor, thus leading to polymerization. On heating to 240°C, the octanolactam alone yields the polymer³¹, within 500 h. In the polymerizations carried out by us and initiated with 1 mol.% of hydrochloride or chromium(III) complex of octanolactam, complete transformation of the monomer is achieved under the same conditions already within 5 h.

Thus, results of X-ray structure analysis along with theoretical calculations show that increased reactivity for nucleophilic substitutions is supported by an increase in the positive charge on the carbonyl carbon atom owing to the coordination of oxygen to the proton or, generally, to a Lewis acid.

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