REACTIONS OF COMPLEXED SMALL NITROGEN HETEROCYCLES

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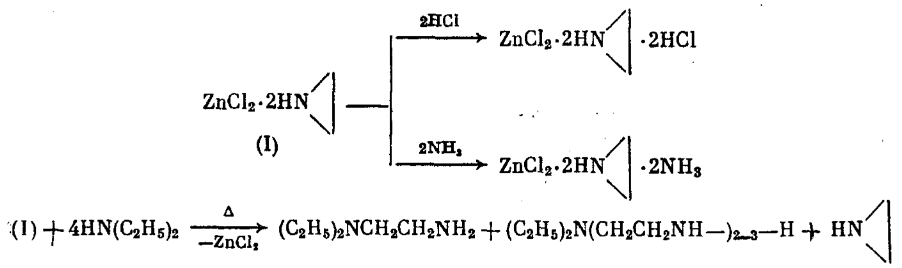
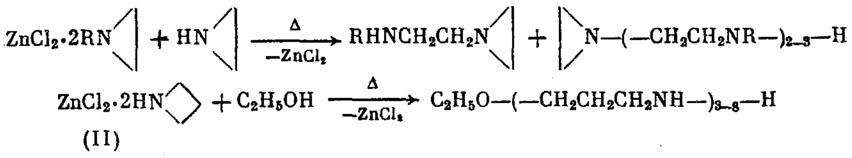
Complexes of ethyleneimine and trimethyleneimine have been examined. Their thermal reactions are strictly controlled, giving polyamine complexes, which can also be obtained directly from the polyamines.

The reactions of organic ligands coordinated in complexes are controlled by the metal ion, and are used in the polymerization of nitrogen heterocycles and other reactions of ethyleneimine (EI) and trimethyleneimine (TMI) complexes [1-4].

We have found that complexes of EI and TMI display dual reactivity, which is governed by the limits of their thermal stability. At temperatures below the limiting values, reactions occur which are characteristic of coordination compounds, namely, exchange or further coordination of the ligands. Above the limiting values, they are supplemented by reactions involving ring cleavage:



In an excess of diethylamine, the reaction proceeds to give yields of less than 10%, and free EI has been isolated from the reaction mixture. In EI, oligomers are formed with a terminal ethyleneimine group, and in excess of alcohols, oligomers with a terminal ether group.



R = H; $(CH_3)_3SiCH_2CH_2$.

These results have been obtained with EI and TMI [4, 5]. Coordinate bonding activates the heterocycle [6]. The thermal stability of the rings has been measured by thermogravimetry, as the onset of exothermic effects on the thermogram. Thermally initiated polymerization of the complexes occurs at 87-135°C. After heating the ampuls containing the complexes at the required temperature in a thermostat, the reaction products were treated with ammonia or caustic alkali, purified on ion-exchange resins, and examined.

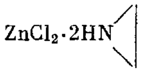
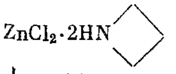
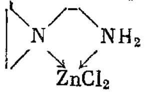
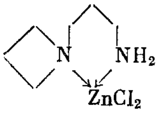
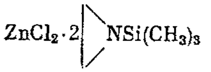
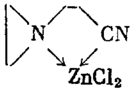
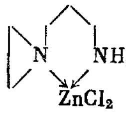
The polymerization of complexes of unsubstituted heterocycles invariably gives branched polyamines:

$$-\left[-CH_2CH_2N(R)-\right]_n-; \quad -\left[-CH_2CH_2CH_2N(R')-\right]_n-$$

$$R = H, CH_2CH_2NH_2;\ R' = H, CH_2CH_2CH_2NH_2.$$

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1108-1114, May, 1990. Original article submitted April 10, 1989.

TABLE 1. Polymerization Conditions and Structural Features of Polyamines

Monomer		T_c^*	T_p^{**}	Relative amounts of primary, secondary, and tertiary nitrogen atoms in propylamines		
		°C		—NH₂	=NH	≡N—
	(I)	125	130	1	0,7	1
	(II)	115	120	1	1,6	1
	(III)	130	135	1	0,8	1
	(IV)	98	110	1	1,2	1
	(V)	75	87	1	1	1
	(VI)	95	107	–	–	1
	(VII)	120	130	1	2	1
	(VIII) ***	350	80	1	2	1
	(IX) ***	350	80	1	5	1

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*T_c is the temperature of cleavage of the heterocycle.

**T_p is the polymerization temperature.

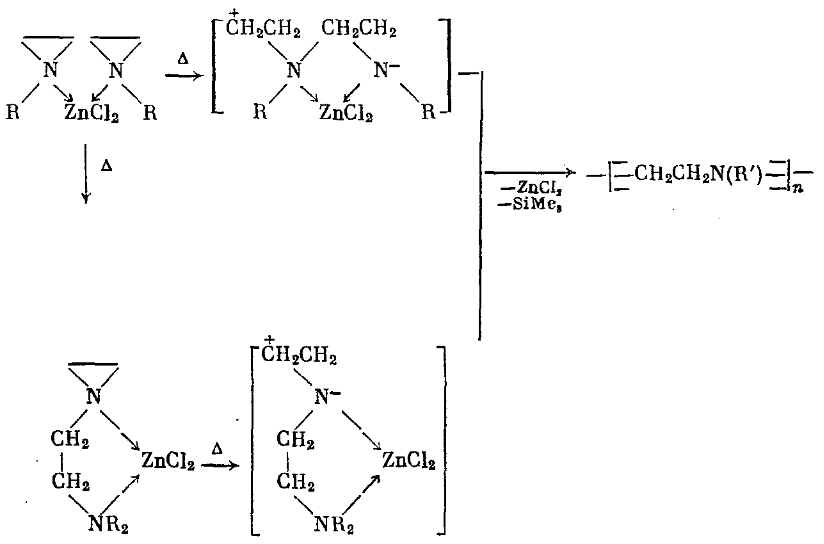
***Polymerization initiated by HCl.

'Protection' of the nitrogen atom with a trimethylsilyl group does not give unbranched polyligands. The polyethyleneimine (PEI) obtained after desilylation contained primary, secondary, and tertiary nitrogen atoms. To establish the reasons for the branching, the compounds obtained in the initial stages of the polymerization of the complexes of EI and TMI with $ZnCl_2$ (I) and (II) were examined. In addition to oligomers, dimers of EI and TMI were found. The possibility of intraspherical dimerization of the ligands on heating the complexes with the cleavage of one heterocycle has been considered in the case of carbonyl complexes of EI [7, 8].

We have synthesized model complexes of N-β-aminoethylethylenediamine and N-γ-aminopropyltrimethyleneimine with $ZnCl_2$ (III) and (IV), and examined their polymerization. It would be expected that polymerization of the complexes (III) and (IV) would give polyamines analogous to those obtained from the complexes (I) and (II). Table 1 shows the ^{13}C NMR data for the extent of branching of the polyamines obtained by the different methods.

In polyamines obtained by cationic polymerization of EI and TMI (VIII) and (IX), the amount of secondary nitrogen present is substantially greater than in those obtained by the thermally initiated polymerization of the complexes, while the polyamines obtained from complexes (I) and (III) contain approximately the same ratios of primary, secondary, and tertiary nitrogen. With (II) and (IV), the proportion of secondary nitrogen is slightly reduced. The experimental findings confirm the assumption that on heating the complexes (I) and (II), intraspherical rearrangement occurs with cleavage of one ring in the complex. The differing amounts of secondary nitrogen in PEI and PTMI may be due to the fact that in the case of TMI the rearrangement proceeds at a lower rate.

It is most interesting that all types of nitrogen atom are present in the product of polymerization of the complex of silylated EI (V). It had previously been assumed that desilylated EI was present even in the original complex (V), as a result of the reaction of N-trimethylsilylethyleneimine with residual water coordinated with the $ZnCl_2$ [9]. However, the water content of the $ZnCl_2$ used in the present work was insignificant, while the polyamine contained approximately equal amounts of primary, secondary, and tertiary nitrogen. It is, therefore, more likely that the polymerization of (V) involves rearrangement, as in the case of unprotected EI. The thermally induced polymerization of the complexes may be shown as follows:



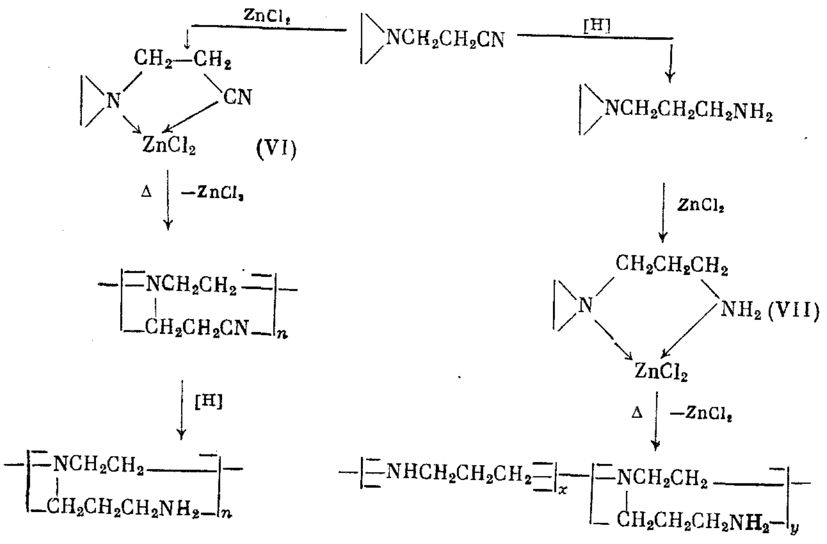
$R = H, -Si(CH_3)_3$; $R' = H, -CH_2CH_2NH_2$.

The involvement of zwitterions in polymerization has been reported [2, 3]. The possibility of the formation of polyamine containing primary, secondary, and tertiary nitrogen has been confirmed by data on the reactions of mixed complexes of EI, primary, and secondary amines [4, 5]. It had previously been shown that the complex of EI and diethylamine forms new complexes at 120°C, which contain N,N-diethylethylenediamine, and dimers and trimers of EI as ligands. This is direct proof of the addition of diethylamine in the complex, as a result of which the polymerization reaction is interrupted. Complexes of $ZnCl_2$ obtained by reacting equimolar amounts of EI and diethylamine (DEA), in fact, consist of a mixture of complexes $ZnCl_2$·EI·DEA, $ZnCl_2$·2EI, and $ZnCl_2$·2DEA. It is this which gives rise to the compounds $(C_2H_5)_2NCH_2CH_2NH_2$, $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2NH_2$, etc., found in the reaction products [4]. The identification of these products shows that coordinated nitrogen atoms with N—H bonds are involved in the formation of polyamines. Rearrangement in the complexes and the involvement of N—H bonds explain the formation of polyligands containing primary, secondary, and tertiary amino-groups in the macromolecular complexes.

Thermally induced polymerization of complexes of EI and TMI cannot give unbranched polyamines, or those containing primary and tertiary nitrogen. However, polymerization of the N-β-cyanoethylethyleneimine complex (VI) followed by reduction of the polymer affords a polyamine containing primary and tertiary amino-groups only. The IR spectrum of the polymer shows absorption at 1580 cm^{-1} (deformational vibrations of NH_2), 3800-3500 cm^{-1} (N—H stretching vibrations in the primary amine), and 1310 cm^{-1} (tertiary amine), but no absorption at 2260 cm^{-1} (C≡N).

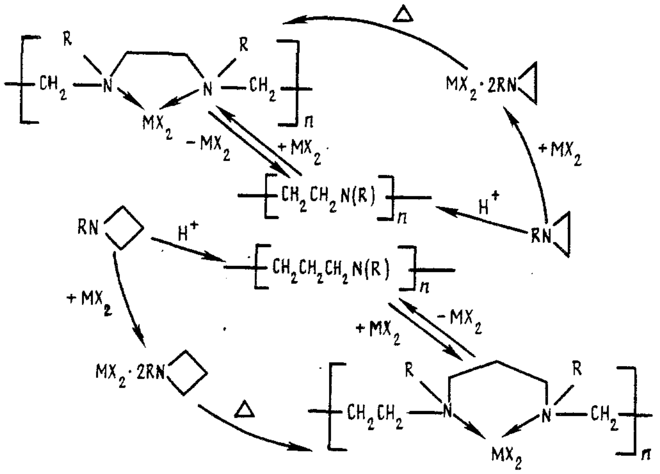
The complex of N-γ-aminopropylethyleneimine (VII), obtained by hydrogenation of N-β-cyanoethylethyleneimine, on thermal polymerization affords a polyamine containing primary, secondary, and tertiary amino-groups in a ratio of 1:2:1.

Thermal polymerization of monomeric complexes can therefore yield a variety of polyamines:



The thermally initiated polymerization of complexes of small heterocycles provides a direct route to macromolecular coordination compounds of polyamines. However, the synthesis of polycomplexes of different compositions is restricted by the number of coordinated heterocycles at the metal in, and by the partial dissociation of the heterocycles during polymerization at elevated temperatures. For example, EI forms complexes with metal chlorides which in general contain not more than four bonded heterocycles, and N-substituted compounds no more than two. The possibility of thermal polymerization is also limited by the coordinated metal. Palladium and platinum chlorides do not form complex macromolecules, since the temperatures at which polymerization occurs are close to those at which the polycomplex is degraded [6, 9].

We have found that complex formation in the system metal—polyamine occurs stepwise, with the successive formation of complexes with N:M ratios of 2, 4, 5, and 6. The polycomplexes obtained in this way contain chelate rings, and may have coordinately unsaturated metal ions [10]. Complex polyamines can react with ammonia, amines, and alkali metal hydroxides, with the formation of free polyamines. The following general scheme shows the reactions leading to the formation of coordinated polyamines.



M = Zn, Ni, Co, Pd; X = Cl, Br.

One of the most important tasks in the creation of macromolecular catalytically active systems is the construction of macromolecular complexes containing transition metals in differing stereochemical environments. The use of polyamines as macromolecular ligands opens up a wide range of possibilities for the preparation of macromolecular catalysts [9, 10].

EXPERIMENTAL

The EI and TMI used were thoroughly dried over caustic alkali, and twice distilled over metallic sodium. The acrylonitrile was dried over potassium carbonate, and twice distilled.

N-Trimethylsilylethyleneimine, bp 94.5-96°C, n_D^{20} 1.4120, was obtained as described in [11]. **N-β-Cyanoethylethyleneimine**, bp 80-84°C (10 mm), n_D^{20} 1.4443, was obtained as in [12]. **N-β-Aminoethylethyleneimine** was obtained as in [13], bp 46-46.5°C (40 mm), n_D^{20} 1.4540.

N-β-Cyanoethyltrimethyleneimine. To 5 g (8 mmoles) of TMI, cooled to –25°C, was added slowly with stirring 4.6 g (8 mmoles) of acrylonitrile. The mixture was stirred for 3 h at ~20°C, and twice fractionated to give 7.68 g (80%) of product, bp 62-64°C (2 mm), n_D^{20} 1.4523. Found: C 66.11; H 9.70; N 24.20%. $C_6H_{10}N_2$. Calculated: C 65.42; H 9.15; N 25.43%. IR spectrum (ν, cm^{-1}): 1240, 910, 980 (TMI ring), 2250 (C≡N); 2950, 2920, 2850, 1475, 1415 (chain CH_2).

N-γ-Aminopropyltrimethyleneimine. To 500 ml of dry ether and 4.05 g of $LiAlH_4$ in a reaction flask was added dropwise with stirring 7.81 g of N-β-cyanoethyltrimethyleneimine. The mixture was stirred for 6 h at 30°C, allowed to stand, and the ether layer decanted and fractionated to give 6.5 g (83%) of product, bp 74-76°C (30 mm), n_D^{20} 1.4600. Calculated: C 63.33; H 12.52; N 24.15%. $C_6H_{14}N_2$. Calculated: C 63.11; H 12.36; N 24.53%. IR spectrum (ν, cm^{-1}): 1240, 910, 980 (TMI ring); 3450, 3380, 3200, 1595, 820 (NH_2); 2950, 2850, 2820, 2920, 1470 (chain CH_2).

Obtained similarly was N-γ-aminopropylethyleneimine from N-β-cyanoethylethyleneimine, bp 63-64°C (40 mm), n_D^{20} 1.4555. Found: C 58.73; H 12.97; N 28.30%. $C_5H_{12}N_2$. Calculated: C 59.95; H 12.08; N 27.99%. IR spectrum (ν, cm^{-1}): 1265, 1445, 2980 (EI ring); 3460, 3380, 3200, 1598, 820 (NH_2); 1040, 1070 (C—N); 2930, 2850, 2820, 1470, 1360 (chain CH_2).

The synthesis of the complexes of EI, TMI, and trimethylsilylethyleneimine with $ZnCl_2$ (I), (II), and (V) have been described [6, 9, 14].

Complex (III). To a solution of 4.2 g (30 mmoles) of $ZnCl_2$ in 150 ml of dry ether, cooled to –20°C, was added slowly with vigorous stirring 2.58 g (30 mmoles) of N-β-aminoethylethyleneimine in 20 ml of dry ether, and the mixture stirred for 4 h at 20°C. The resulting colorless solid was isolated, washed with ether, and dried in vacuo to give 5.83 g (86%) of product. Found: C 21.9; H 4.70; N 12.0%. $C_4H_{10}N_2 \cdot ZnCl_2$. Calculated: C 21.6; H 4.53; N 12.6%. IR spectrum (ν, cm^{-1}, KBr): 1253, 990, 910 (EI ring); 3280, 3222, 1585, 715 (NH_2); 2935, 2880, 1460 (chain CH_2); 275 (Zn—Cl); 460, 370 (Zn—N).

Complex (VI). To a solution of 6.8 g (50 mmoles) of $ZnCl_2$ in 150 ml of dry ether, cooled to –20°C, was added slowly with vigorous stirring 4.8 g (50 mmoles) of freshly distilled N-β-cyanoethylethyleneimine in 20 ml of dry ether, and the mixture stirred for 4 h at 20°C. The resulting colorless solid was filtered off, washed with dry ether, and dried in vacuo to give 10.8 g (93%) of product. Found: C 25.94; H 4.06; N 11.28%. $C_5H_8N_2 \cdot ZnCl_2$. Calculated: C 25.84; H 3.5; N 12.05%. IR spectrum (ν, cm^{-1}, KBr): 1253, 993, 910 (EI ring); 2260 (C≡N); 2950, 2920, 2880, 1405 (chain CH_2); 280 (Zn—Cl); 370 (Zn—N).

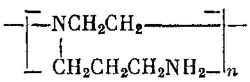
Obtained similarly was **Complex (IV)**. Found: C 28.3; H 5.2; N 10.4%. $C_6H_{14}N_2 \cdot ZnCl_2$. Calculated: C 28.8; H 5.6; N 11.2%. IR spectrum (ν, cm^{-1}, KBr): 1245-1252, 970, 900 (TMI ring); 3280, 3230, 1585, 720 (NH_2); 2950, 2850, 1465, 1360-1370 (chain CH_2); 290 (Zn—Cl); 380, 460 (Zn—N).

Obtained similarly was **Complex (VII)**. Found: C 25.8; H 4.76; N 12.42%. $C_5H_{12}N_2 \cdot ZnCl_2$. Calculated: C 25.4; H 5.1; N 11.85%. IR spectrum (ν, cm^{-1}, KBr): 1253, 1445 (EI ring); 3280, 3230, 1585, 720 (NH_2); 2940, 2880, 1465 (chain CH_2); 280 (Zn—Cl); 460, 390 (Zn—N).

Cationic polymerization of EI and TMI was carried out in the presence of 3 mole % of HCl at 80°C for 24 h [13, 15]. The resulting polyamines had $[\eta]_{PEI} = 0.13$, $[\eta]_{PTMI} = 0.16$.

The polymerization of complexes (I), (II), and (V), and the isolation of the polyamines, have been described [6, 9, 14, 15]. A similar method was used to polymerize complexes (III), (IV), (VI), and (VII), and to isolate the polyamines formed (Table 1).

Hydrogenation of Poly-(N-β-cyanoethyl)ethyleneimine. In a 50 ml autoclave were placed 1 g of poly-(N-β-cyanoethyl)ethyleneimine, 20 ml of ethanol, and 0.01 g of Raney nickel. Hydrogenation was carried out for 8 h at 95 atm and 80°C. The solvent was then distilled off, and the polymer dried in vacuum to constant weight. Found: C 59.68; H 12.38; N 27.94%. Calculated: C 59.96; H 12.07; N 27.97%. The IR spectrum of the polymer showed no absorption at 2260 cm^{-1} (CN). The poly-(N-γ-aminopropyl)ethyleneimine, in contrast to the analogous polymer obtained by the thermally induced polymerization of complex (VII), contained no secondary amino groups. The polymer obtained was a macromolecule with the elementary unit



$$\left[-\underset{\displaystyle CH_2CH_2CH_2NH_2}{\underset{|}{N}}CH_2CH_2-\right]_n$$

Thermogravimetric studies were carried out with an MOM derivatograph, systems F. Paulik, I. Paulik, and L. Erdei, over the temperature range 20-500°C. The rate of heating was 10°C/min, and the DTA and DTG sensitivity 1/10. Weighed samples of 0.1-0.2 g were heated in air in a platinum crucible, endo- and exothermic effects being recorded as DTA plots, and the weight loss of the sample as TG and DTG plots.

IR spectra were obtained on Perkin-Elmer and UR-20 spectrophotometers in KBr disks and vaseline oil, and as microlayers, over the range 200-3500 cm^{-1}.

^{13}C NMR spectra were recorded on a Bruker WP-8C spectrometer (20.115 MHz).

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