Polycondensation versus metal template condensation of 2,2'-ethylenedithiodianiline with glyoxal

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SUMMARY:

A polymer with azomethine linkages is formed upon reaction of 2,2'-ethylenedithiodianiline (1) with glyoxal. The same reaction in the presence of Ni(II) and Cu(II) ions yields the corresponding metal complexes of the macrocyclic ligand. The driving force for the selectivity of this reaction may be attributed to the template effect of the metal ions. In the case of Co(II) ions, the polymer is formed as a by-product, together with the macrocyclic complex.

Introduction

Metal-oriented or so-called "metal template" condensations are of great importance because of their role in the preparation of macrocyclic ligands in high yields. There have been numerous examples ¹⁾ of transition metal catalyzed macrocyclization involving 1,3-dienes or acetylenes alone or with appropriate olefins. In these cases macrocyclization occurs between metal π -complexed olefins. On the other hand, there are few reports on the macrocyclization arising from the reaction the coordinated ligands with another reagent. Perhaps the most significant efforts on the subject can be attributed to Bush²⁾, Curtis³⁾ and Tasker et al.⁴⁾. Certainly, the stereochemical relationship of the ligand to metal ion contributes to the stability and yield of the resulting macrocyclic complexes. We have previously observed⁵⁾ that in the reaction of acenaphtoquinone with two moles of *o*-aminophenol only one of the two carbonyl groups is converted to the azomethine group. Similar reaction in the presence of Co(II), Ni(II) and Cu(II) ions, which are capable of forming square-planar coordination complexes, produced the corresponding metal complexes of the compound possessing bisazomethine groups.

Metal template reactions are also widely used for the synthesis of crown ethers⁶ and cyclams⁷, which can selectively bind alkali and transition metal ions, respectively. On the other hand, macrocyclic ligating molecules receive attention not only for their metal binding capability but also for the stabilization of metal ions in unusual oxidation states⁸ such as Cu(III).

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In this paper a study was made of some of the condensation reactions of 2,2'-ethylenedithiodianiline (1) with glyoxal in the presence and absence of transition metal ions, leading to cyclization or polymerization, respectively.

Experimental part

Materials and methods: All solvents and chemicals used in the experiments were obtained commercially and were of reagent grade. They were used without any further purification. IR spectra were recorded on a Perkin Elmer model 577 spectrometer with KBr discs. Mass spectra were taken using a LKB type 9000S with electron impact (70 eV) by a direct insertion probe. ¹H NMR spectra were obtained using a Bruker 270 MHz spectrometer and DMSO-d₆ as solvent (tetramethylsilane (TMS) internal standard). Thermogravimetric measurements were made on a Perkin Elmer TGS-2 analyser under nitrogen flow with 10 °C/min heating rate. Viscosity measurements were performed by using a Desreux-Bishoff suspended level viscosimeter in DMF solution at 30 ± 0,01 °C. GPC chromatograms were obtained using a Knauer M 64 instrument with THF as eluent and flow rate of 1 ml \cdot min⁻¹. Molecular weights were calculated by reference to polystyrene standards.

Preparation of 2,2'-ethylenedithiodianiline (1): A solution of 25 g (0,2 mol) of 2-aminothiophenol in 50 ml of ethanol was placed in a three-necked flask equipped with a reflux condenser, a dropping funnel and a nitrogen inlet. A solution of 8 g (0,2 mol) of NaOH in 10 ml of water was added with stirring under nitrogen. The mixture was heated for 30 min, and 9,9 g (0,1 mol) of 1,2-dichloroethane in 50 ml of ethanol was added dropwise in about 1 h. The mixture was then refluxed for 3 h and left overnight. The content of the flask was poured into water, and the precipitate was filtered off and washed with water. The crude product was recrystallized from benzene. Yield: 23,5 g (81,5%); m. p.: 75 °C (lit.⁹⁾: m. p. 76 °C).

Polymerization: 1,66 ml of a 30% glyoxal solution (0,01 mol) was added to a solution of 2,76 g (0,01 mol) of 1 in 50 ml of ethanol. The mixture was stirred at room temperature for 1 h, then refluxed for an additional hour. An oligomeric waxy product was formed which was dissolved in 50 ml of N,N-dimethylformamide (DMF). Ethanol was removed from the solution by evaporation, and the clear solution was refluxed for another hour. The mixture was left overnight at room temperature and no precipitation occurred. A yellow-brown product settled down upon pouring into water. After decanting the water, the precipitate was boiled in ethanol. In hot ethanol, the polymer melted and gave a fibrous material, which on cooling solidified and became brittle. Finally polymer 4 was dried at room temperature i. vac. Yield: 2,42 g (81%); m. p.: $80-110^{\circ}$ C; $\eta = 0,105$ dl/g in DMF at 30 °C; polymer degradation temperature: 334° C.

Complexation of 1: To a hot solution of 2,76 g (0,01 mol) of 1 in 50 ml of ethanol 0,01 mol of MtCl₂ · H₂O in 50 ml of ethanol was added with stirring. The colour of the mixture gradually changed within a few minutes. Upon heating under reflux for 1 h, a coloured precipitate was formed in the cases of Ni(II) and Cu(II), whereas a green colour but no precipitate appeared in the case of Co(II), regardless of the conditions. The precipitate of complex 2 was filtered off, washed successively with ethanol and diethyl ether, and dried i. vac. at room temperature. MS (70 eV) of Cu complex 2: m/z = 276, 312, 320, 322, 334, 310.

Macrocyclization: 5 mmol of Ni(II) or Cu(II) complex 2 were dispersed in 40 ml of ethanol. While stirring at reflux temperature, 0,8 ml of a 30% solution of glyoxal (5 mmol) were added dropwise in 90 min. The colour of the complex darkened during the reaction. The reflux was continued for another 2 h. The hot mixture was filtered, the precipitate washed with ethanol and diethyl ether, and finally dried i. vac. Yield was 1,3 g (61%) for the Ni complex and 1,47 g (70%) for the Cu complex. The solution of the corresponding cobalt complex gave both macrocyclic complex and polymer under the same reaction conditions. The polymer was extracted from the crude product by dispersing in 60 ml of boiling DMF. This procedure was repeated three times (yield: 0,3 g (20%)), and the remainder was essentially macrocyclic cobalt complex (yield: 0,56 g (26%)). Similar yields were obtained when the macrocyclization reactions were performed in situ, i.e., without isolation of the complexs of type 2. MS (70 eV) of Ni complex 3: m/z = 276, 296, 301, 303, 360, 361, 372.

Results and discussion

The direct interaction of 1 with glyoxal results in the formation of a linear polymer (4), whereas in the presence of transition metal ions the reaction gives the corresponding metal complexes of the macrocyclic ligand. Scheme 1 represents the overall reactions. Ethanol was found to be a suitable solvent for the polymerization experiments, but the formed polymer was subsequently dissolved in DMF for further





purification. The gel permeation chromatographic trace of a typical polymer is shown in Fig. 1. Interestingly, if the procedure was repeated in DMF as solvent, only an insoluble dark product was obtained. This may be attributed to substitution reactions between glyoxal and the phenyl ring of 1, which consequently results in crosslinking. The following experimental and spectral evidence confirms the proposed structures.



Fig. 1. GPC trace of polymer 4 (numberaverage mol. wt. $\overline{M}_n = 1640$, weight-average mol. wt. $\overline{M}_w = 4400$, $\overline{M}_w/\overline{M}_n = 2,68$)

IR spectra

Characteristic IR bands of the compounds are tabulated in Tab. 1. After complexation, the N—H stretching and bending vibrations of 1 become broad, as expected. In

Compound ^{a)}	Elemental analysis Found (Calc.)			m.p. in °C	Characteristic IR bands in cm ⁻¹
	C%	H%	N%		
1	59,96 (60,37)	5,92 (5,79)	9,78 (10,14)	75	3 380 (NH (sym); sharp) 3 295 (NH (asym); sharp) 1 608 (NH (plane); y sharp)
1-Ni complex	41,32 (41,58)	4,27 (3,96)	6,61 (6,93)	>300	3 370 - 3 460 (NH; broad) 1 605 (NH; broad)
1-Cu complex	39,08 (40,33)	3,82	6,73 (6,75)	>300	3 380-3 460 (NH; broad) 1 605 (NH; broad)
MC-Ni complex	45,34 (44,89)	3,27 (3,37)	7,03	>300	1 660-1 640 (C=N; broad)
MC-Cu complex	44,52 (44,39)	3,23	6,37 (6,47)	>300	1 660 (C=N; broad)
MC-Co	43,87	3,56	6,38 (6,54)	>300	1 660 (C=N; broad)
Polymer	63,57 (63,42)	4,71 (4,70)	9,11 (9,39)	105-115	1 660 (C=N; broad)

Tab. 1. Analytical and spectral data for the related compounds

a) MC: Macrocyclic compound.

the IR spectra of the polymer and macrocyclic complexes, the N—H vibrations of 1 disappear and the characteristic broadened bands of the C=N group are observed in the range 1600-1660 cm⁻¹.

NMR spectra

The NMR spectra of the structurally related compounds are shown in Figs. 2-5. In the ¹H NMR spectrum of the polymer 4 (Fig. 3) a triplet corresponding to the -CH=N- protons appears at 1,1 ppm and the singlet corresponding to the NH₂ protons of 1 at 5,3 ppm disappears. This fact indicates that the reaction proceeds via condensation of the aldehyde and amine groups to form the azomethine linkage. In other words, no substitution occurs on the phenyl ring by glyoxal, which was evidenced additionally by the observation of the same splitting patterns of the aromatic protons in both the polymer and 1. In order to see the effects of complexation on the NMR signals of both 1 and the macrocyclic ligand, and to confirm the proposed structures, their nickel(II) complexes were deliberately chosen, since square-planar nickel(II) complexes are diamagnetic. In the NMR spectrum of the nickel complex of 1 (Fig. 4) all the peaks are broadened and drastically shifted to lower fields. This means that the complex is paramagnetic and consequently the type of coordination around the nickel(II) ion is tetrahedral, as in the case of well-known examples in the literature¹⁰. It is interesting to note that after the ring closure step, the broad singlet protons of the



Fig. 2. ¹H NMR spectrum of 1. $\delta = 6,4-7,2$ ppm (multiplet, aromatic protons), $\delta = 5,3$ ppm (singlet, $-NH_2$); $\delta = 2,8$ ppm (triplet, $S-(CH_2)_2-S$)



Fig. 3. ¹H NMR spectrum of polymer 4. $\delta = 6,4-7,4$ ppm (multiplet, aromatic protons); $\delta = 2,5-3,3$ ppm (multiplet, S-(CH₂)₂-S); $\delta = 1,05$ ppm (triplet, =HC-CH=)



Fig. 4. ¹H NMR spectrum of the nickel complex of 1 (2, Mt = Ni). $\delta = 7,7-8,7$ ppm (multiplet, aromatic protons); $\delta = 6,1$ ppm (broad singlet, $-NH_2$); $\delta = 4,2$ ppm (broadened triplet, S--(CH₂)₂-S)

amine group at 6,06 ppm disappear and all of the remaining peaks return to almost their original position (Fig. 5). This clearly reveals that the macrocyclic nickel complex is diamagnetic and the structure of the complex is planar in contrast to the former case.



Fig. 5. ¹H NMR spectrum of the nickel complex of the macrocyclic compound (3, Mt = Ni). $\delta = 6,3-7,2$ ppm (multiplet, aromatic protons); $\delta = 3,4$ ppm (broadened singlet, =CH-CH= protons between N atoms); $\delta = 2,8$ ppm (triplet, S-(CH₂)₂-S)

In this connection, it should be noted that ligand 1 has much more flexibility with respect to the macrocyclic ligand, and the free rotation facility around the ethylene bridge between the S atoms in 1 allows a tetrahedral rearrangement. Whereas in the macrocyclic ligand the structure is sterically forced to be planar by sp^2 hybrids of the azomethine groups. However, the peaks of the -CH=N- protons do not appear around 1 ppm but appear at 3,2 ppm as broadened ethylene bridge signals. A similar shift of azomethine protons was reported by Bayer et al. for *a*-diimines¹¹ and for glyoxal bis(mercapto anils)¹².

Metal extraction experiments

We attempted to obtain the metal-free macrocyclic ligand by the ligand exchange method. For this purpose, metal complexes of the macrocyclic ligand were treated with a saturated solution of KCN, a strong complexing agent. All of the experiments at different temperatures and in different solvents, including direct reduction with LiAlH₄, failed and 1 was reformed resulting from the hydrolysis of the macrocyclic compound. This behaviour may be attributed to the promotion effect ¹⁾ of metal ions on hydrolysis.

Mass spectra

In order to establish the macrocyclic structure, we compared the mass spectra of the nickel complex of the macrocyclic ligand and the 1-copper complex. However, molecular ions of the macrocyclic metal complexes were not observed, but their primary fragment ions were. In the mass spectra of all compounds m/z = 276 is the parent ion, which corresponds to the molecular ion of 1. And, surprisingly, the macrocyclic complex does not show an m/z = 298 ion, which corresponds to the organic part of the macrocyclic metal complex; instead, the m/z = 296 peak appears. On the other hand, the m/z = 368 and 370 ions, which result from the invisible

molecular ion (at m/z = 426 and 427) by elimination of the nickel atom, were recorded. According to these results, the following fragmentation pattern may be proposed: First, nickel atom elimination occurs from the molecular ion, and a macrocyclic ligand compressing two chlorine atoms is formed showing signals at m/z = 368 and 370. Similarly, the corresponding ion in the cobalt complex appears at m/z = 372. Certainly, the kind of structural rearrangement which causes the stabilization of the two chlorine atoms is not clear. However, in the next step, the elimination of two HCl molecules gives the m/z = 296 fragment ion, and C_2Cl_2 elimination gives the m/z = 274 ion. In the case of the copper complex of 1, the mass spectrum is quite simple; elimination of CuCl from the invisible molecular ion gives the m/z = 311 ion, and elimination of CuCl₂ gives the m/z = 276 ion, which is the parent ion. Fragmentation then continues according to a pattern typical of the organic part.

Conclusions

The following conclusions can be drawn from the experimental results obtained:

i) Direct interaction of 1 with glyoxal yields a polymer.

ii) Soluble Co(II) complex of 1 gives both macrocyclic and polymeric products with glyoxal.

iii) Addition of glyoxal together with metal ions to a solution of 1 gives almost the same results for Ni(II) and Cu(II) ions. At the first stage, formation of a precipitate of 1/metal complex can be followed visually. The colour of the mixture then gradually changes and macrocyclization occurs. This indicates that complexation of 1 with metal ions is much faster than condensation with glyoxal. This behaviour can be assigned to the decreased nucleophilicity of the coordinated amine groups¹³⁾. Here, the role of

Scheme 2:







Chelation in macrocyclic structure (ncr = 4)





Chelations between two different polymer chains (ncr = 2)

(ncr = number of chelate rings)

metal ions is a template effect which can be considered as "kinetic template", since cyclization depends on the solubility of the 1-metal complex. The reaction tends to cyclization due to lower solubilities of the nickel and copper complexes, which provides conditions similar to high dilution. However, in the present case, the thermodynamic contribution of template effect should also be taken into account. The polymer can also give metal complexes, yielding a totally insoluble product when a stoichometric amount or an excess of metal ions is used, although they are different from those of its macrocyclic counterparts with respect to their colour and number of chelate rings (ncr). The nickel complex of the polymer is brown, whereas the nickel complex of the macrocyclic structure is thermodynamically much more favourable than the polymeric structures possessing two or three chelate rings according to intra- or intermolecular interaction, as depicted in *Scheme 2*. This causes a preference towards cyclization.

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