Journal of Inclusion Phenomena 5 (1987), 153–156. © 1987 by D. Reidel Publishing Company.

SYNTHESIS OF SYMMETRICAL N-TOSYLDIAZAMACROCYCLES AND COMPLEXATION PROPERTIES OF THEIR DERIVATIVES

Sebastiano Pappalardo, Francesco Bottino Dipartimento di Scienze Chimiche, Università di Catania Viale A. Doria 8, 95125 Catania, Italy

Paolo Finocchiaro\*, Antonino Mamo Istituto Chimico, Facoltà di Ingegneria, Università di Catania Viale A. Doria 6, 95125 Catania, Italy

Frank R. Fronczek Department of Chemistry, Louisiana State University Baton Rouge, LA 70183-1804

## 1. INTRODUCTION

Synthetic azamacrocycles have attracted considerable attention in recent years because of their ability to selectively bind both metal [1] and organic ammonium cations [2].

We have recently developed a general synthetic procedure which offers an easy access to a variety of multifunctional N-tosylazamacrocycles (azacrown ethers, azacyclophanes, and azaheterophanes) [3]. Detosylation of these materials has afforded multifunctional (poly)aminomacrocycles, which have proved to be a suitable matrix for structurally defined polycondensates. As a result, two novel polyamide ligands 7 and 8, containing cyclic or acyclic bipyridinediyl diamino units 5 and 6 in the polymer backbone, have been prepared and their complexing properties towards bivalent ions of the first transition series explored [4].





## 2. RESULTS

The synthesis of symmetrical multifunctional N-tosylazamacrocycles  $\underline{4}$  has been accomplished by coupling readily available bis(halomethyl) or bis (tosylate ester) compounds 1 with two equiv of tosylamide monosodium salt (TsNHNa) in anhydrous dimethylformamide (DMF) under moderate dilution. The reaction is best envisioned as proceeding through the monoalkylated key intermediate 2, which quickly undergoes self-condensation (path A) in the presence of an excess of TsNHNa to give the desired 1:1 (n=0) and/or 2:2 (n=1) macrocycles. Alternatively, 2:2 macrocycles can arise from the N,N'-ditosyl intermediate 3 through path B (Scheme 1).



Detosylation of 4 to the corresponding (poly)aminomacrocycles was effected by conc.  $H_2SO_4$  or Na/liquid NH $_3$ .

Polymers  $\underline{7}$  and  $\underline{8}$  were obtained by polycondensation of the appropriate diamino-precursor with one equiv of terephtaloyl chloride in anhydrous chloroform. Model compounds  $\underline{5c}$  and  $\underline{6c}$  were synthesized by similar

routes.

Complexation of models 5c and 6c as well as of polyamides 7 and 8 with Co(II), Ni(II), and Cu(II) has been achieved. The ligands and their complexes have been characterized by conventional techniques. The  $[Co(\underline{6c})](NO_3)_2 \cdot 2H_2O$  complex has been further characterized by a single

crystal X-ray analysis.

## 3. CONCLUSIONS

 $^{1}$ H-VTNMR analysis on macrocyclic diamide <u>5c</u> indicates a fixed <u>syn</u> conformation in solution, with a 'face to face' arrangement of the dipyridinyl moieties, as shown in Fig. 1.



Fig. 1. The syn conformation of compound 5c.

Model compound <u>6c</u> and polyamide <u>8</u> form stable 1:1 complexes with transition metals Co(II), Ni(II), and Cu(II). Conversely, macrocyclic model <u>5c</u> and polyamide <u>7</u> exhibit the unique property to specifically complex Cu(II) even in the presence of sizeable amounts of Co(II) and Ni(II).

The IR data show that Co(II) and Ni(II) complexes exhibit a large shift (55-60 cm<sup>-1</sup>) of the carbonyl absorption to lower frequencies, strongly suggesting that the carbonyl groups are involved in the complexation; in sharp contrast, the C=O frequency band is not affected in the Cu(II) complexes, indicating for the latter different binding sites.

According to the IR data, the single crystal X-ray structure determination of  $[Co(\underline{6c})](NO_3)_2.2H_2O$  indicates an octahedral environment around the complex cation, as shown in Fig. 2. The square planar coordination positions are occupied by the bipyridine nitrogens and by the two carbonyl groups, while two water molecules reside at the axial positions.



Fig. 2. ORTEP drawing of  $[Co(6c)](NO_3)_2.2H_2O$  complex

Acknowledgement. The authors gratefully acknowledge the Ministero della Pubblica Istruzione (Fondi 40%) for partial support of this work.

## References

- J. J. Christensen, D. J. Eatough, and R. M. Izatt: <u>Chem. Rev. 74</u>, 351 (1974); J. D. Lamb, R. M. Izatt, and J. J. Christensen: '<u>Chemistry of Macrocyclic Compounds</u>', ed. by G. Melson, Plenum Press, New York 1979.
  J. M. Lehn and P. Vierling: <u>Tetrahedron Lett</u>. 1323 (1980).
- 3. S. Pappalardo, F. Bottino, M. Di Grazia, P. Finocchiaro, and A. Mamo:
- Heterocycles 23, 1881 (1985).
- 4. S. Pappalardo, F. Bottino, P. Finocchiaro, and A. Mamo: J. Polym. Sci., Polym. Chem. Edn., in press.