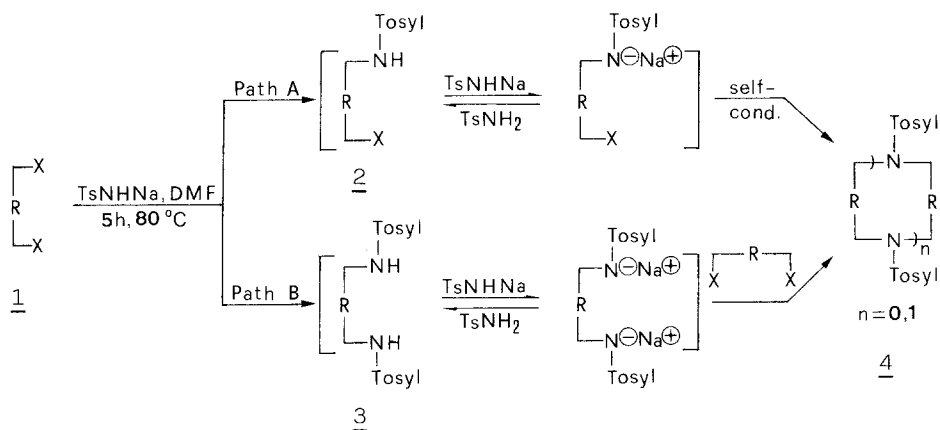


2. RESULTS

The synthesis of symmetrical multifunctional *N*-tosylazamacrocycles 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).



Scheme 1

Detosylation of 4 to the corresponding (poly)aminomacrocycles was effected by conc. H_2SO_4 or Na/liquid NH_3 .

Polymers 7 and 8 were obtained by polycondensation of the appropriate diamino-precursor with one equiv of terephthaloyl chloride in anhydrous chloroform. Model compounds 5c and 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(6c)](NO₃)₂·2H₂O complex has been further characterized by a single crystal X-ray analysis.

3. CONCLUSIONS

¹H-VTMR analysis on macrocyclic diamide 5c indicates a fixed syn conformation in solution, with a 'face to face' arrangement of the dipyridinyl moieties, as shown in Fig. 1.

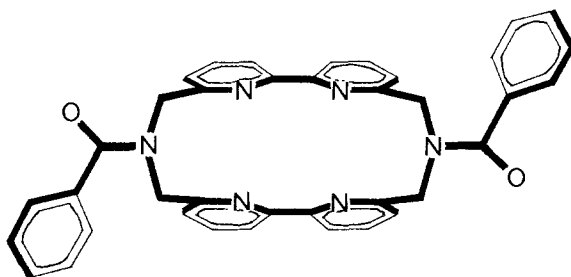


Fig. 1. The syn conformation of compound 5c.

Model compound 6c and polyamide 8 form stable 1:1 complexes with transition metals Co(II), Ni(II), and Cu(II). Conversely, macrocyclic model 5c and polyamide 7 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⁻¹) 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(6c)](NO₃)₂·2H₂O 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.

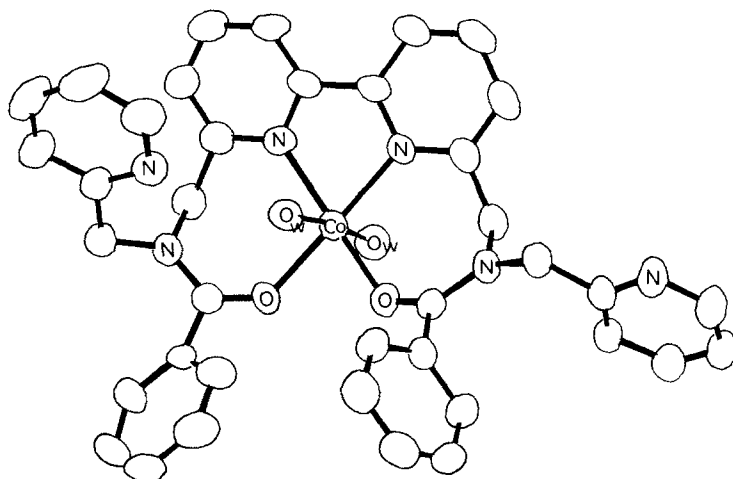


Fig. 2. ORTEP drawing of $[\text{Co}(\underline{6c})](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ complex

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References

1. J. J. Christensen, D. J. Eatough, and R. M. Izatt: Chem. Rev. **74**, 351 (1974); J. D. Lamb, R. M. Izatt, and J. J. Christensen: 'Chemistry of Macrocyclic Compounds', ed. by G. Melson, Plenum Press, New York 1979.
2. J. M. Lehn and P. Vierling: Tetrahedron Lett. 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.