

A Thermodynamic and Electronic Explanation of the Macrocyclic Effect

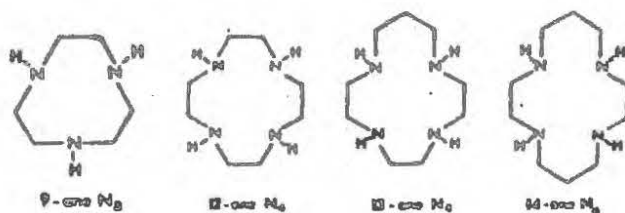
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The extra stability of the complexes of macrocyclic ligands over that of their open-chain analogs has been termed the macrocyclic effect [1]. In addition to the extreme thermodynamic stability, macrocyclic complexes display a stronger ligand field than do their open-chain analogs, provided that the "hole" is not too large for the metal ion [2].

Based upon the ligand field splitting parameters for various tetraaza macrocyclic complexes of cobalt and nickel, D. H. Busch originally suggested that the high ligand fields were due to compression of the metal ion [3]. Recent empirical force-field calculations on complexes of the macrocyclic ligands shown below were carried out and the results show the compression hypothesis to be incorrect. Rather, it appears a though the largest ligand field is obtained for the macrocycle which bonds to the metal ion with the least strain in the metal-nitrogen bond [4].



Gas phase enthalpy data [5] clearly show the greater inductive effects of secondary nitrogens relative to primary ones. It is believed that the increased ligand field strength of the macrocycle over the open-chain analog is due to this increased inductive effect of the extra secondary nitrogens found in the macrocyclic ligand [6].

The thermodynamic stability of tetraaza macrocyclic complexes seems to have contributions both enthalpic and entropic in origin. It is generally agreed that the entropy contribution arises from the smaller configurational entropy of the macrocycle, and it is the enthalpy contribution that requires explanation [4].

The inductive effect of the secondary nitrogens is a contributor to the macrocyclic enthalpy. Empirical force-field calculations carried out by R. D. Hancock also shows that steric "pre-straining" of the macrocyclic ligand contributes to the macrocyclic enthalpy [6]. Thermodynamic studies on mixed-donor macrocycles of oxygen and nitrogen [7], and sulfur and nitrogen [8] show that this pre-straining may be modified by steric hindrance to solvation in aqueous solution. This evidence is not conclusive however.

An interesting property of tetraaza macrocycles appears to be an anomalous metal ion size selectivity [9]. Very large metal ions complex most strongly to a relatively small macrocycle (12-aneN₄), while smaller metal ions prefer an intermediate sized macrocycle (14-aneN₄) [10]. The reason for this phenomenon

is shown by molecular mechanics calculations to be due to the ability of the tetraaza macrocycles to adopt various conformations upon complexation to the metal ion [11].

References

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