ing basicity order holds: DMPz > Pz > DMPPz. Additional evidence in support of this sequence was also obtained from conductivity measurements . On the other hand, for each one of the ligands under consideration, the experimentally observed overall stability trend is: $CoBr_2L_n > CoI_2L_n > CoCl_2L_n$. It is perhaps worth noting that taking into account only the strength of the Lewis acids the expected stability order would be: $CoI_2L_n > CoBr_2L_n > CoCl_2L_n$. However, looking exclusively at the ionic radii of the halides the reverse order would be observed, owing to steric hindrance. The higher overall stabilities associated with the $CoBr_2L_n$ systems could be ascribed to a best compromise between the two aforementioned opposite effects. For the most part of these systems unusual stability patterns are found (*e.g.*, $K_4 > K_3$) suggesting possible changes in the mode of formation of the complex species as the number of coordinated ligands is increased [1, 3].

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## Solvent and Ligand Interactions with the Ni(II) and Cu(II) Complexes of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

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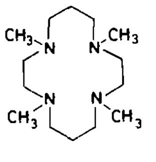
1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (L) forms metal complexes of different geometries at the metal ion and different configurations at the nitrogens [1].



L

Many of these complexes interact with solvent molecules or with ligands forming ternary species $MLX^{2+}$ (eqn. 1)

$$ML^{2+} + X \overset{K_{MLX}}{\rightleftharpoons} MLX \tag{1}$$

The Ni(II) complex with the *trans*-I (R,S,R,S) nitrogen configuration is especially interesting since it is tetra- or penta-coordinate. In poor donor solvent such as acetone square planar geometry is found, in water a mixture of the square planar and the penta-coordinate forms is found, whereas in DMF the penta-coordinate species predominates.

Addition of unidentate ligands such as $SCN^-$, $OCN^-$, $N_3^-$, $F^-$, $I^-$, $OH^-$ and $NH_3$ to $NiL^{2+}$ in any of the solvents mentioned gives mixed complexes with penta-coordinate geometry. The stability of these have been measured by spectrophotometric titrations with an on-line computer [2]. Similar experiments with $CuL^{2+}$ in different solvents and with several ligands have also been carried out. All the Cu(II) complexes exhibit penta-coordination of the metal ion, thus being similar in this respect to the Ni(II) compounds.

The results indicate that the mixed complexes with the small and linear ligands such as $SCN^-$, $OCN^-$ and $N_3^-$ have the highest stabilities. Larger molecules such as pyridine and imidazole do not bind to the metal ion. This is a consequence of the steric interaction of the larger ligands with the four methyl groups of the macrocycle in its *trans*-I(R,S,R,S) configuration.

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## Patterns in Lewis Acid–Base Interactions in Aqueous Solution

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The observable patterns in free energies of complex-formation in aqueous solution have lead to many