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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References

1 C. Melios, M. Molina, H. Yamanaka and J. O. Tognolli, *Proc. IV Int. Symp. Solute–Solute–Solvent Interactions*, Vienna (1978) pp. 208–210.

2 M. Molina, C. Melios, A. C. Massabni and T. Takaki, *J. Coord. Chem.*, *7*, 133 (1978).

3 S. Ahrland, *Pure and Appl. Chem.*, *51*, 2019 (1979).

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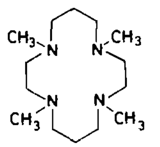
1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (L) forms metal complexes of different geometries at the metal ion and different configurations at the nitrogens [1].



L

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

$$ML^{2+} + X \overset{K_{MLX}}{\rightleftharpoons} MLX \qquad (1)$$

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.

References

1 E. K. Barefield and F. Wagner, *Inorg. Chem.*, *12*, 2435 (1973); R. Buxtorf and Th. Kaden, *Helv. Chim. Acta*, *57*, 1035 (1974); R. Buxtorf, W. Steinmann and Th. Kaden, *Chimia*, *28*, 15 (1974); M. J. d'Aniello, M. T. Mocella, F. Wagner, E. K. Barefield and I. C. Paul, *J. Am. Chem. Soc.*, *97*, 192 (1977); N. W. Alcock, N. Herron and P. Moore, *J. Chem. Soc. Dalton*, 1282 (1978).

2 G. Hänish, Th. A. Kaden and A. D. Zuberbühler, *Talanta*, *26*, 563 (1979).

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

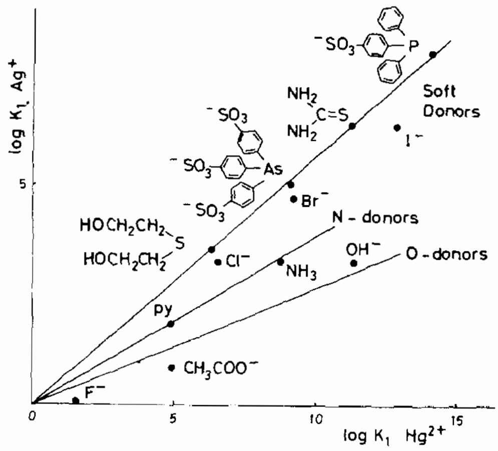

Fig. 1. LFER diagram for Ag^+ *vs.* Hg^{2+}.

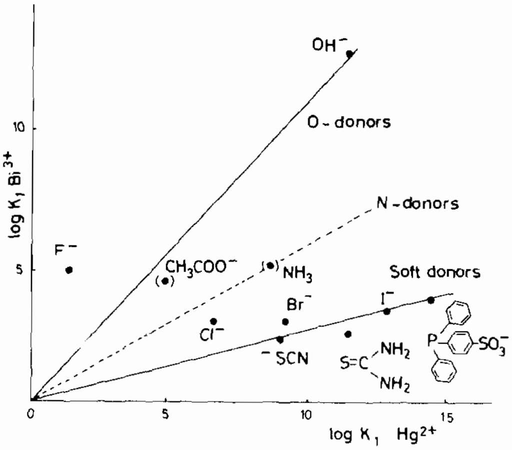

Fig. 2. LFER diagram for Bi^{3+} *vs.* Hg^{2+}.

classifications (A and B, 'hard' and 'soft) of Lewis acids and bases. These can be illustrated with LFER (linear free energy relationship) diagrams [1]. Figure 1 is consistent with Pearson's ideas on hard and soft acids and bases (which are interpreted as representing ionic and covalent bonding) if Ag(I) is softer than Hg(II). Figure 2 displays the same pattern as Fig. 1, but is inverted, indicating that Bi(III) is harder than Hg(II). These patterns, which are similar for all metal ions, may be reproduced using eqn. 1, which is essentially that due to Drago and coworkers [2].

$$\log K_1 = E_AE_B + C_AC_B \tag{1}$$

E and C are the tendency of the Lewis acid A and base B to undergo ionic and covalent bonding. Eqn. 1 is not able to correlate formation constants for complexes of ligands having large donor atoms (S, P, As, Cl, Br, I) with smaller Lewis acids (Cu(II), Co(III), the proton), but works well for small ligands (F^-, OH^-, NH_3) with all Lewis acids. The deviations from the prediction of eqn. 1 are interpreted as being due to (*i*) steric hindrance to solvation of the Lewis acid by large donor atoms, and (*ii*) specific solvation effects, which operate through the increased softness induced in the Lewis acid by attachment of very soft donor atoms. Mechanism (*i*) is supported by evidence from correlations in the NMR and infra-red involving the structural *trans* effect, while mechanism (*ii*) is supported by results on proton-basicities of organic bases in the gas-phase.

Eqn. 1 is extended to give eqn. 2, which correctly predicts the formation constants of 266 different

$$\log K_1 = E_AE_B + C_AC_B - D_AD_B \tag{2}$$

complexes involving 31 different Lewis acids (including the proton) with 16 different unidentate bases. The D parameters are identified with desolvation effects arising from mechanism (*i*) and (*ii*) above.

References

1 R. D. Hancock and F. Marsicano, *Inorg. Chem., 17,* 560 (1978).
2 R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc., 93,* 6014 (1971).

A Thermodynamic Study on Oxygen Carrier Complexes. The System Co(II)–Ethylenediamine (*en*)–O_2

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Resulting from two recent comprehensive reports [1, 2], much attention has been devoted to the complexes named 'oxygen carriers'. However, a critical examination of the tables there reported for the enthalpy and entropy changes connected to the oxygenatin reaction allows us to recognize a very unsatisfactory situation: (*i*) the ΔH and ΔS values are in general very few and limited almost exclusively to Co/O_2 = 1:1 complexes and only four data have been reported for Co/O_2 = 2:1 complexes, (*ii*) most of the enthalpy data have been obtained using the indirect method of studying the dependence of the equilibrium constant on temperature, (*iii*) no agreement has been reached in the choice of the standard states and the free energy and the entropy data reported for different systems are often not directly