aqueous solution, can nonetheless be prepared using other solvents.

Finally, in relation to the *Macrocyclic Effect,* I want to show you how careful we chemists need to be. One of the first, and very popular hypotheses, which was formulated about the origin of the stability of macrocyclic complexes was based on a ΔH° value obtained from the temperature dependence of the appropriate stability constant. It was concluded that the origin of this enhanced stability derived from the smaller solvent-interaction of macrocyclic as opposed to non-cyclic ligands. To-day, this attractive hypothesis is recognized as only one of the possible contributions to this extra stability and this change has essentially been brought about by the direct calorimetric determination of the enthalpies of formation of macrocyclic metal complexes, revealing gross discrepancies from the ΔH° values obtained by indirect route, of which a criticism has already been levelled.

Thermodynamics of Complex Formation with Multidentate Ligands

G. ANDEREGG

Laboratorium für Anorganische Chemie, E.T.H.Z, Universitätstrasse 6, CH-8091 Zurich, Switzerland

Complex formation in solution is generally described by a reaction of type I. This formulation does not correspond to what actually takes place, namely

$$M^{z+} + L^{n-} \rightarrow ML^{(z-n)+} \qquad \text{I}$$

process II, because of the omission of the solvent as

$$M(H_2O)_q^{z+} + L(H_2O)_m^{n-} \rightarrow ML(H_2O)_p^{(z-n)+} + (q + m - p)\,H_2O \qquad \text{II}$$

reacting partner. Indeed the entropy of complex formation is generally positive and large, depending strongly on the dentateness of the ligand, and not negative as it would be expected for reaction I, because of the decrease of the number of species in solution. The influence of the solvent seems also to be reflected in the value of the enthalpy of complex formation: for complexes with multidentate charged O-ligands it is generally not very different from zero. This is because the endothermic effect for the dehydration of the reacting species is almost compensated by the exothermic effect of the ligand coordination. On the contrary, for neutral ligands, the enthalpy is remarkably negative as result of (*1*) the lower hydration of the ligand, (*2*) the covalency of the bonding, and (*3*) no charge neutralisation occurs.

In multidentate ligands the donor atoms connected together by chains which, on complex formation, give rise to chelate rings. These are considered responsible for the higher stability of complexes with multidentate ligands with respect those of monodentate ligands, if in the complexes the same number of donor atoms are involved. The interpretation of this effect, the *Chelate Effect,* has been the subject of active discussion over the last thirty years and it is still a matter of opinion. In this connection, one should consider not only for five-, six- and seven-membered chelate rings a positive *Chelate Effect* is observed. If there are more than six atoms between the donor atoms or chelating units, their neutral influence decreases and eventually reduces to that of a statistical effect.

The values of the enthalpy and of the entropy for complex formation with the same ligand and a series of related metal ions, such as the alkaline earth, the 3d divalent metal or the 4f trivalent lanthanide ions can be correlated with stereochemical and electronic effects at the central ion such as the dentateness of the ligand, the coordination number of the metal ion and ligand field effects.

The formation of mixed (ternary) complexes will be also considered in some detail. These have recently received more attention, especially because of their increased stability with respect to that expected by statistical consideration and in relation of their importance in biological systems.

The Macrocyclic Effect in Tetraaza-Macrocyclic Ligands

ROBERT D. HANCOCK* and GLORIA J. McDOUGALL

National Institute for Metallurgy, Randburg, South Africa

The origin of the Macrocyclic Effect [1] in complexes of *cyclam* as compared with those of its open-chain analogue *2,3,2-tet* is discussed. It is not readily apparent that the presence of four secondary (2°) nitrogens in *cyclam,* as opposed to two primary (1°) and two 2° in *2,3,2-tet* should make much difference, since the pK_a's of 2° amines are not much different from those of 1°. Proton basicity in water is a misleading guide to base-strength. For example, $\log K_n$-(RNH_2) with Ag(I) increases strongly as R changes

TABLE I.

NiL_n,	L = *en*	*pn*	en_3	*dien*	$dien_2$	*tetren*	*2,3,2-tet*	*cyclam*
ΔU	0.61	2.14	0.80	4.04	6.70	11.06	3.33	1.33
$-\Delta H$, calc:	8.99	7.46	28.00	12.06	2.55	18.04	19.27	24.67
$-\Delta H$, obs:	9.0	7.8	28.0	11.9	2.53	18.3	19.2	24.1

in the order R = Me < Et < *i*-propyl < *t*-butyl, although the pK_a's are almost invariant. This effect is attributable to greater steric hindrance to solvation for the proton. For 1° *versus* 2° nitrogens, it is found in the gas phase, for example, that $(CH_3)_2NH$ is a much stronger base than CH_3NH_2, although their pK_a's in water are identical. This effect is partly attributable to quenching of polarizability effects [2], and also steric hindrance to solvation. The E and C equation of Drago and Wayland [3] is used to show that in the absence of steric effects, the Cu–N bond in $[Cu(Hfac)_2NRR'_2]$ is stronger by 3.3 kcal mol^{-1} when NRR'_2 is $(CH_3)_2NH$. This qualitative suggestion that the M–N bond is stronger when N is 2° is supported [4] by empirical force field calculations of the increase in conformational potential energy, *U*, on complex-formation of Ni(II) with a variety of polyamine complexes. In each case, *U* has been calculated for each of the species in the reaction below, allowing calculation of ΔU.

$$\begin{array}{ccccc} M & + & L & \overset{\Delta U}{\rightleftarrows} & ML \\ U_M & & U_L & & U_{ML} \end{array}$$

It was found that consistency could only be obtained by making the 2° Ni–N bond 1.7 kcal mol^{-1} more exothermic than the 1°. If a value of 4.8 kcal mol^{-1} is accorded to the ideal Ni–N bond to a nitrogen in the absence of steric strain, summation of the appropriate number of contributions from 1° and 2° nitrogens followed by subtraction of ΔU allows one to calculate $-\Delta H$ as shown in the Table. All calculations are for the high-spin complexes. From these results, one may assign the macrocyclic enthalpy to, firstly the presence of more 2° nitrogens in *cyclam*, followed by a smaller ΔU than is found for *2,3,2-tet*. An important point in favour of these ideas which suggests stronger Ni–N bonds, is that 10 Dq for the Ni(II) *cyclam* complex is higher than for *2,3,2-tet*. Contributions of solvation and entropy effects to the macrocyclic effect are discussed. Results below are in kcal mol^{-1}.

References

1 F. P. Hinz and D. W. Margerum, *J. Am. Chem. Soc., 96,* 4993 (1974).

2 R. W. Taft, in 'Kinetics of Ion-molecule Reactions', P. Ausloss Ed., Plenum Press, New York (1979).

3 R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc., 87,* 3571 (1965).

4 R. D. Hancock, G. McDougall and F. Marsicano, *Inorg. Chem.*, in press.

Some Properties of Macrocyclic Complexes in Solution which are Related to the Ligand Ring Size

LUIGI FABBRIZZI

Istituto di Chimica Generale e Laboratorio C.N.R., Università di Firenze, Florence, Italy

The relation between the structural features of ligands and the properties of their metal complexes, which has been generally observed in coordination chemistry, is demonstrated dramatically in the case of tetra-aza macrocycles. In particular, solution properties of macrocyclic complexes (thermodynamic and kinetic stabilities, redox behaviour, spin-state equilibria) are strongly dependent on the size of the ligand cavity. For instance, in the formation of Ni(II) and Cu(II) complexes with a series of 12- to 16-membered cyclic tetramines, the most exothermic reactions occur with the 14-membered ring; expansion or contraction of the ligand cavity results in a substantial decrease of the enthalpy of formation, up to 60%. Likewise, the electrode potential values for the Ni(II)/Ni(III) couple, for the same macrocyclic systems, show a completely analogous ring size dependence: the attainment of the +3 state is easiest for the symmetric 14-membered ligand and becomes progressively more difficult by either an increase or decrease in size of the ligand cavity (up to 0.4 V). This behaviour seems to be related to the strength of the in-plane metal–macrocycle interactions, which in turn derive from the relative compatibility between the geometrical features of the ligand and the electronic requirements of the transition metal ion, in the appropriate oxidation state.