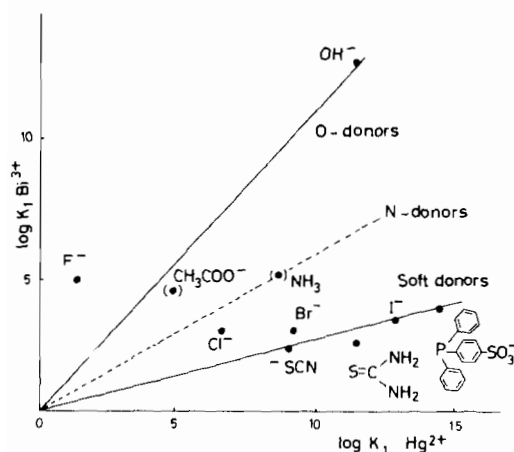Fig. 1. LFER diagram for Ag⁺ *vs.* Hg²⁺.

Fig. 2. LFER diagram for Bi³⁺ *vs.* Hg²⁺.

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].

$$\log K_1 = E_A E_B + C_A C_B \qquad (1)$$

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

$$\log K_1 = E_A E_B + C_A C_B - D_A D_B \qquad (2)$$

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.

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A Thermodynamic Study on Oxygen Carrier Complexes. The System Co(II)–Ethylenediamine (*en*)–O₂

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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/O₂ = 1:1 complexes and only four data have been reported for Co/O₂ = 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

comparable with each other, (iv) when data for the same system, studied by different authors, are referred to the same standard state and temperature and then compared, the logK values usually differ for one, two and more unities.

As a part of a program of a systematic study of the thermodynamic and kinetic aspects of the reversible oxygen addition to Co(II) complexes and the successive irreversible oxidation to Co(III) species, we report here the results of a study on the system Co(II)–en–O_2 in aqueous solution at 25 °C (KCl 1 M). Other studies concerning the Co(II)–tetren–O_2 and Co(II)–cyclam–O_2 systems have been undertaken together with the Paoletti and Micheloni of the Florence University and the results obtained will be successively reported.

The thermodynamic and kinetic aspects of the reaction between Co$(en)_2^{++}$ complex and oxygen have been very carefully studied by Miller et al. [3], Nakon et al. [4], Powell et al. [5] and Zehnder et al. [6]. Nakon and Powell agree about the formation of a μ-peroxo-μ-hydroxo complex, but the stability constant calculated from data of Nakon (K = $10^{6.4}$ M^{-1}) differs by three orders of magnitude in respect to that of Powell (K = $10^{10.8}$ M^{-1}). Miller and Zehnder agree that after the fast reaction of the oxygenation a slow process follows, but they do not agree as to what this process is. Finally the enthalpy data obtained from Powell by calorimetry, are criticizable for the way they have been calculated.

By comparing the enthalpy changes measured by means of a liquid flow differential micro calorimeter and an isoperibolic calorimeter, we have been able to give a more complete picture of the mechanism of the oxygenation reaction, with respect to that given by Miller and Zehnder, by identifying as a relatively slow step the passage from the μ-peroxo to the μ-peroxo-μ-hydroxo complex. For both these products of the oxygenation, the enthalpy and the free energy changes associated to their formation have been determined. The former by a proper analysis of the calorimetric curves collected in a large range of pH and en/Co(II) ratios, the latter by recording at the same time the variations of both the hydrogen and the molecular oxygen concentration when known quantities of Co(II) are added to aqueous solutions of en differing in pH and amount of this ligand.

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Investigation on Complexation of Ni(II) with Sulphonated Azo-dyes

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The coordination reactions between Ni(II) and two water–soluble azo-dyes containing respectively the heterocyclic rings tetrazole and thiazole are described. The investigation was performed in 0.1 M NaClO$_4$ aqueous solution, at T = 25.0 °C, with the spectrophotometric method. For each solution, characterized by a constant value of the metal-ion and ligand concentration, the acidity was varied with small additions of concentrated HClO$_4$ or NaOH over the $-$log range 2–6, and for each $-$log value, the spectra were recorded. The functions A vs. $-$log were analyzed with the graphical method described by Sommer [1], so that molar absorbances, compositions and stability constants of each complex could be determined.

The following results have been obtained:

Ligand		
1,8-dihydroxy-naphthalen-2-thiazolato-3,6-disulphonic acid (TAAC) [2]	Ni + HL $\rightleftarrows$ NiHL	log K$_f$ = 2.41 ± 0.03
	2Ni + L $\rightleftarrows$ Ni$_2$L	log K$_f$ = 11.06 ± 0.06
1,8-dihydroxy-naphthalen-2-tetrazolato-3,6-disulphonic acid (T-azo-C) [3]	Ni + HL $\rightleftarrows$ NiHL	log K$_f$ = 7.86 ± 0.03

The molar compositions have been confirmed with Job's method [4].

Some other data on the coordination of Ni(II) with a sulphonated azo-dye in aqueous solution have been previously published [5], and the present work extends the research to other ligands of the same kind.