Thermodynamics of the Interactions of Catechol with Transition Metals. Part II.[1] Copper and Nickel Complexes of Catechol

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Thermodynamic quantities for the formation of copper(II) and nickel(II) complexes of catechol have been determined in 0·100M-KNO_3 background electrolyte at 25 °C. Calorimetric determinations have been made for formation of the 1 : 1 copper complex of catechol, but this was not possible in the case of nickel owing to oxidation of the ligand.

PART I[1] reported the investigation of the ionisation of catechol with the determination of corresponding thermodynamic quantities. The present paper reports a continuation of this investigation with the further determination of thermodynamic quantities for metal complex formation. Although values of the stability constants for these complexes have been reported[2] they were not precise and have been redetermined.

EXPERIMENTAL

Apparatus and Techniques.—The calorimeter, potentiometric assembly, and techniques have been described.[1,3] Copper(II) and nickel(II) ions were titrated with catechol with solutions of ligand and metal in the ratio 2·5 : 1 respectively. This was a precaution against the possible formation of hydroxo-complexes and, in the case of copper, titrations were continued until the 2 : 1 complex was completely formed (in the case of nickel some oxidation occurred towards the end of the titration). Calorimetric determinations of heats of neutralisation of copper–ligand mixtures were made by the use of a batch method since a titration technique introduced a time lag during which extensive oxidation of the ligand occurred. A 50 cm^3 aliquot portion of the ligand solution and then 50 cm^3 of a copper sulphate solution were pipetted into the calorimeter both solutions having been purged with nitrogen; it was ensured that the concentration of ligand was well in excess of that of the metal ion. The reaction was effected by breaking an ampoule of KOH solution into the solution, the usual precautions being taken to exclude CO_2. Solutions of the reactants contained sufficient KNO_3 so that the final ionic

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[1] Part I, R. F. Jameson and M. F. Wilson, preceding paper.

[2] L. G. Sillén and A. E. Martell, 'Stability Constants of Metal-ion Complexes,' *Chem. Soc. Special Publ.*, No. 17, 1964.

[3] R. F. Jameson and M. F. Wilson, *J.C.S. Dalton.*, **1972**, 2607.

strength of the calorimetric solution was 0·100M. The pcH of the solution was determined at the end of the reaction by use of a calibrated Radiometer GK 2025B glass–calomel combination electrode. Since the volume of KOH added was known accurately, the volume of the calorimeter solution after reaction was also known.

Preparation and Analysis of Materials.—Copper solutions were made up from AnalaR copper sulphate pentahydrate which was first moistened and allowed to equilibrate under reduced pressure in a desiccator with the monohydrate. Stock copper solutions were analysed by the salicylaldoxime method.[4] The compound was found to be 99·98% $CuSO_4,5H_2O$. Nickel solutions were made up from AnalaR nickel(II) sulphate and analysed for metal by the dimethylglyoxime method;[4] several determinations on aliquot portions taken from a stock nickel solution agreed to within 0·08%. Catechol and solutions of nitric acid and potassium hydroxide were prepared as in Part I.[1] AnalaR potassium nitrate was used.

RESULTS

Stability Constants for the Copper and Nickel Complexes.—Formation curves for these complexes were obtained from potentiometric titration data and steps occurred in the curves at values of $\bar{n} = 1$ and 2 corresponding to the formation of the complexes ML and ML_2 and involving the loss of two protons per ligand molecule.

A range of metal concentrations all gave a good fit on one theoretical curve and this ruled out the possibility of polynuclear species; also since, in the case of copper at least, $\bar{n}$ never rose above 2, it was assumed that no 3 : 1 or higher complex was formed (oxidation occurred towards the end of the nickel titrations so it was not possible to make similar observations in this case).

Stability constants for the formation of the complexes were calculated with the computer programme LETAGROPVRID.[5,6] The master variables $\bar{n}$ and [L] are related by expression (1), hence the input data were the triplets

$$\bar{n}[M_T] = \Sigma n\beta_n^{M}[M][L]^n \qquad (1)$$

($\bar{n}$, pL, $[M_T]$) for each point of the formation curve, where $pL = -\log_{10}$ [L] and $[M_T]$ = total metal concentration. The overall stoicheiometric stability constants β_1^M and β_2^M were computed and hence the corresponding values of log K_1^M and log K_2^M were obtained. The constants were varied during the computation process and the output was of values which gave the best fit to the data together with their standard deviations. Values of stability constants are in Table 1.

TABLE 1

Stoicheiometric stability constants of copper(II) and nickel(II) complexes of catechol at 25 °C and ionic strength 0·100M (KNO_3), with standard deviations

Metal	log K_1^M	log K_2^M
Copper	13·827 ± 0·002	10·921 ± 0·003
Nickel	8·927 ± 0·012	5·561 ± 0·020

Calorimetric Results for Copper Complex Formation.—The reaction studied by calorimetry was the neutralisation (2) which is analogous to titration of a mixture of the metal and ligand species with base (an excess of ligand was used to

$$H_2L + Cu^{2+} + 2OH^- \rightleftharpoons CuL + 2H_2O \qquad (2)$$

prevent hydrolysis of the metal ion). In these determinations it was necessary to correct the observed heat of reaction for contributions due to the heat of formation of water and heat of dilution of the added base. The enthalpy change for the formation of water in the medium used (0·100M-KNO_3) has been determined (see Part I [1]) and has the value −56·48 kJ mol^{-1} at 25 °C; the correction could therefore be calculated by determining the change in hydrogen-ion concentration, *i.e.*, $\Delta[H^+]$, for the reaction. Separate determinations were carried out to obtain values for the heat of dilution of the added base.

The amount of complex formed in solution was calculated from the metal–ligand stability constant, the proton dissociation constants of the ligand, and the pcH of the solution after reaction; hence the enthalpy change for reaction (2) could be calculated. The proportions of metal, ligand, and added base could be adjusted so that only the 1 : 1 complex was formed, and therefore in all calculations the concentration of the complex ML_2 was taken equal to zero.

The method of calculation was as follows. Since the total metal concentration $[M_T]$ is given by equation (3), then equation (4) follows, where K_1^M is the stability constant

$$[M_T] = [M] + [ML] \qquad (3)$$

$$[M_T] = \frac{[ML]}{K_1^M[L]} + [ML] \qquad (4)$$

for formation of the first complex. Thus the total concentration of the free ligand [L] is given by equation (5). The

$$[L] = \frac{[ML]}{K_1^M([M_T] - [ML])} \qquad (5)$$

total concentration of the ligand $[L_T]$ may be written as in equation (6). Substitution of (5) into (6) and multiplying

$$[L_T] = [ML] + \beta_2^H[H]^2[L] + \beta_1^H[H][L] + [L] \quad (6)$$

out gives an equation quadratic in [ML] and hence the concentration of the complex after reaction can be determined. From the value of [ML], the enthalpy change for the neutralisation reaction, ΔH_n, was calculated.

Using the value of ΔH_n together with other previously determined thermodynamic data we could calculate enthalpy changes for a series of equilibria. Thus, from the value of the enthalpy change for the formation of water in 0·100M-KNO_3, ΔH^* for equilibrium (7) was calculated. Since the

$$Cu^{2+} + H_2L \rightleftharpoons CuL + 2H^+ \qquad (7)$$

equilibrium constant, K_1^*, for reaction (7) was known, it was also possible to obtain corresponding values of ΔG^* and ΔS^*.

Similarly, using thermodynamic quantities for the ionisation of catechol (Part I [1]) we found the corresponding values for reaction (8), and since a less accurate value of the

$$Cu^{2+} + HL^- \rightleftharpoons CuL + H^+ \qquad (8)$$

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[4] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 1961.

[5] L. G. Sillén, *Acta Chem. Scand.*, 1964, **18**, 1085.

[6] N. Ingri and L. G. Sillén, *Arkiv Kemi*, 1964, **23**, 97.

enthalpy change for ionisation (9) has also been obtained by

$$HL^- \rightleftharpoons H^+ + L^{2-} \qquad (9)$$

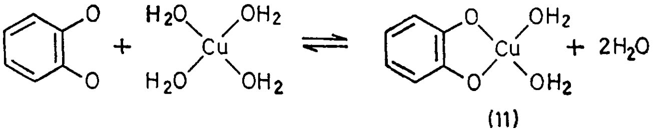
the temperature-coefficient method (where L^{2-} represents the catecholate anion), only approximate values of thermodynamic constants for equilibrium (10) could be determined.

$$Cu^{2+} + L^{2-} \rightleftharpoons CuL \qquad (10)$$

Several determinations of the enthalpy change for neutralisation (2) were carried out by use of ligand concentrations within the range $6{\cdot}194 \times 10^{-3}$—$1{\cdot}189 \times 10^{-2}$M and copper concentrations $2{\cdot}478 \times 10^{-3}$—$4{\cdot}757 \times 10^{-3}$M. The resulting mean value of ΔH_n is $-99{\cdot}59 \pm 0{\cdot}80$ kJ mol^{-1} and of ΔH^* $13{\cdot}39 \pm 0{\cdot}80$ kJ mol^{-1}. Thermodynamic quantities for various equilibria involving the formation of the 1 : 1 copper(II) complexes with catechol are given in Table 2.

DISCUSSION

Initially one of our principal objectives was to obtain precise values of thermodynamic quantities for formation of the 1 : 1 copper–catechol complex from the deprotonated ligand and the aqueous copper(II) ion, as given by reaction (10). This reaction can be represented in greater detail by (11) (ionic charges are omitted). However, in order to determine thermodynamic quantities for reaction (11), it is essential that very precise values of the enthalpy changes for the ionisation of both protons of the catechol ligand be known accurately. Although such values for the first proton ionisation have been determined,[1] the enthalpy change for the second ionisation could not be determined calorimetrically owing to interference by oxidation of the ligand, and only an approximate value could be determined by the temperature-coefficient method. However, precise thermodynamic quantities for reactions (7) and (8) were obtained and these are in Table 2; since it is expected that oxidation of catechol-type ligands will interfere in future work, it seems that correlation of thermodynamic data will be based on information from reactions of the type (7) and (8), although some guide may be obtained from the less accurate values given in Table 2 for reaction (10).



(11)

The problem of oxidation in the case of complex formation with nickel is even more marked, no calorimetric determination being possible. It is possible that in the case of nickel less accurate values may be determined in the future by the temperature-coefficient method.

The thermodynamics of complex formation have been discussed by Ahrland [7] in terms of ' hardness ' and ' softness '. Both of the ions Cu^{2+} and Ni^{2+} are classified as borderline cases in the hard and soft acid and base classification, whereas catechols may be classified as hard bases. Complexes of soft donors (*e.g.*, CN^-) are formed in strongly exothermic reactions and are ' enthalpy-stabilised ' with counteracting negative entropy terms. Hard donors (*e.g.*, F^-) form complexes in endothermic reactions and are usually referred to as ' entropy-stabilised '. In the case of the copper(II)–catechol complex, it appears that the enthalpy and entropy terms both make large contributions to the free-energy change for complex formation, both terms favouring reaction.

TABLE 2

Thermodynamic quantities for the formation of the copper(II)–catechol complex at 25 °C and ionic strength 0·100M (KNO_3)

$Cu^{2+} + H_2L \rightleftharpoons CuL + 2H^+$

log K_1^*	ΔG^*/ kJ mol^{-1}	ΔH^*/ kJ mol^{-1}	ΔS^*/ J K^{-1} mol^{-1}
$-8{\cdot}345 \pm 0{\cdot}009$	$47{\cdot}66 \pm 0{\cdot}04$	$13{\cdot}39 \pm 0{\cdot}80$	-115 ± 2

$Cu^{2+} + HL^- \rightleftharpoons CuL + H^+$

log K_1^M	ΔG/ kJ mol^{-1}	ΔH/ kJ mol^{-1}	ΔS/ J K^{-1} mol^{-1}
$0{\cdot}85 \pm 0{\cdot}01$	$-4{\cdot}85 \pm 0{\cdot}04$	$-20{\cdot}9 \pm 0{\cdot}8$	-54 ± 2

$Cu^{2+} + L^{2-} \rightleftharpoons CuL$

log K_1^M	ΔG/ kJ mol^{-1}	ΔH/ kJ mol^{-1}	ΔS/ J K^{-1} mol^{-1}
$13{\cdot}827 \pm 0{\cdot}002$	$-78{\cdot}93 \pm 0{\cdot}04$	-42	-130

In general, little work has been done in determining thermodynamic quantities for metal-complex formation in aqueous solution involving ligands with hydroxy-groups as potential bonding sites. Arhland suggested [7] that in certain cases hydroxy-groups may well be bonded to the metal ion *via* water molecules. In the case of the catechols, solvation effects are expected to have a marked influence on complex formation owing to the presence of the *ortho*-diphenol grouping. It is possible that complete desolvation of the bonding sites on the ligand may not take place on complex formation, and the complexes may consist of solvent-separated species.

[2/999 *Received, 4th May,* 1972]

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[7] S. Ahrland, *Helv. Chim. Acta*, 1967, **50**, 306.