Thermodynamics of the Interactions of Catechol with Transition Metals. Part III.[1] The Effect of 4-Chloro- and 4-Nitro-substitution on Proton and Metal Catechol Complex Formation

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The effect on proton and metal complex formation of substitution of chloro- and nitro-groups in the catechol 4-position has been investigated by potentiometric, calorimetric, and spectrophotometric methods with 0·100M-KNO_3 as background electrolyte at 25 °C. Thermodynamic quantities for complex formation have been determined and some interpretation of the effect of substitution on bonding has been made.

PREVIOUS investigations in this laboratory of proton and metal complex formations with 4-substituted catechols have been concerned mainly with catecholamine ligands having side-chains which are essentially 'electron-donating' substituents.[2,3] The ligands adrenaline and L-Dopa are characteristic. We now report a study of the effect on complex formation of electron-withdrawing substituents in the catechol 4-position.

EXPERIMENTAL

Apparatus and Techniques.—The potentiometric assembly, treatment and calibration of glass electrodes, and preparaion of silver–silver chloride electrodes were described.[4] The LKB 8700 Precision Calorimeter was tested by means of the THAM reaction [5] and heats of neutralisation of the ligands were measured as in Part I.[6] The method for the determination of heats of neutralisation of metal–ligand mixtures was described in Part II [1] and a batch method was used since titration introduced a time lag during which chlorocatechol was oxidised. Nitrocatechol was stable to oxidation under these conditions provided that pcH was not above 9·5. Copper(II) and nickel(II) ions were titrated with the ligands with a ligand : metal ratio of 2·5 : 1 as a precaution against the formation of hydroxo-complexes. Spectrophotometric determinations were made with a Unicam SP 700 spectrophotometer.

4-Nitrocatechol (Puriss; Ralph Emmanuel Ltd.) was 98·27% pure by potentiometric titration with KOH. 4-Chlorocatechol (Aldrich) was twice purified [charcoal in light petroleum (b.p. 60—90 °C)] and recrystallised, and was then triply sublimed; potentiometric titrations indicated better than 99·9% purity. The preparation of solutions of copper and nickel and potassium hydroxide titrant was described in Part II.[1] AnalaR potassium nitrate was used.

RESULTS

Dissociation Constants of the Ligands.—For each ligand a serious of titrations was carried out and the average number of protons, g, abstracted from the ligand was calculated by use of the previously determined value of the ionic product of water.[4] Dissociation constants were calculated by the computer programme LETAGROPVRID.[7,8] Dissociation constants of the first and second proton ionisations of the ligands are in Table 1. The results are compared with corresponding values for catechol determined in previous work.

Stability Constants of Copper(II) *and Nickel*(II) *Complexes.*—These were obtained from potentiometric titration data and formation curves were also plotted revealing steps at values of $\bar{n} = 1$ and 2 corresponding to the formation of complexes of the type ML and ML_2. By using a range of metal concentrations it was established that no polynuclear complex was formed. Stability constants were calculated again by use of the computer programme LETAGROPVRID, the input data being the master variables $\bar{n}$ (the average number of ligands bound per metal), pL (−log[free ligand]), and $[M_T]$ the total metal concentration. The output data were values of the overall stoicheiometric stability constants β_1^M and β_2^M and from these the corresponding values of log K_1^M and log K_2^M were found; standard deviations were also computed and these are given with stability constant values in Table 2.

TABLE 1

Acid dissociation constants of the catechol ligands, together with standard deviations, measured in an ionic background of 0·100M-KNO_3 at 25 °C

Ligand	$-\log K_1^a$	$-\log K_2^a$
Catechol	9·195 ± 0·002	12·98 ± 0·01 *
4-Chlorocatechol	8·522 ± 0·002	11·974 ± 0·007
4-Nitrocatechol	6·701 ± 0·002	10·853 ± 0·004

* Part I.

Calorimetric Results for the Ionisation of the Ligands.—As in the case of catechol,[6] at pcH values as low as 8·8 oxidation of 4-chlorocatechol occurred and interfered with the determination of the enthalpy change for the second ionisation; hence only the first ionisation of the ligand could be investigated by calorimetry. Similarly some decomposition of 4-nitrocatechol was detected, but only at high pcH values.

Heats of neutralisation of the ligands, Q_n, were determined calorimetrically by neutralisation (1) with potassium

$$H_2L_{(aq)} + OH^-_{(aq)} \longrightarrow HL^-_{(aq)} + H_2O \qquad (1)$$

hydroxide. Corrections were made for the heat of formation of water,[6] Q_w (which was dependent upon the concentration of the excess of acid in the calorimeter solution) and also for the heat of dilution of the added base Q_{dil}.

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

[2] R. F. Jameson and W. F. S. Neillie, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2623.

[3] R. F. Jameson and J. E. Gorton, *J. Chem. Soc.* (*A*), 1968, 2615.

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

[5] R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, 1964, **18**, 195.

[6] Part I, R. F. Jameson and M. F. Wilson, *J.C.S. Dalton*, 1972, 2610.

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

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

Hence the uncorrected measured heat of reaction Q_r, was given by equation (2).

$$Q_r = Q_{dil} + Q_w + Q_n \qquad (2)$$

The concentration of ionised ligand after reaction was determined from the known pK_1^a value and the final hydrogen-ion concentration; hence the enthalpy change, ΔH_n, for the first proton neutralisation of the ligands was calculated. The corresponding enthalpy change for the first proton ionisation was given by expression (3).

TABLE 2

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

Ligand	$\log K_1^M$	$\log K_2^M$	$\Delta = \log K_1^M - \log K_2^M$
	Copper(II)		
Catechol	13·827 ±0·002	10·921 ±0·003	2·906 *
4-Chlorocatechol	12·894 ±0·002	10·163 ±0·003	2·731
4-Nitrocatechol	11·666 ±0·004	9·282 ±0·005	2·384
	Nickel(II)		
Catechol	8·927 ±0·012	5·561 ±0·020	3·37 *
4-Chlorocatechol	8·375 ±0·014	5·467 ±0·018	2·19
4-Nitrocatechol	7·887 ±0·005	5·504 ±0·008	2·38

* Part II.

$$\Delta H_{ion} = \Delta H_n - \Delta H_w \qquad (3)$$

Results for the calorimetric determination of ΔH_n and ΔH_{ion} are given in Table 3 together with standard deviations. Thermodynamic quantities for the first proton ionisation of the ligands are summarised in Table 4.

TABLE 3

Calorimetric results for the enthalpy changes of the first proton neutralisation and ionisation of 4-chloro- and 4-nitro-catechol at 25 °C and ionic strength 0·100M (KNO_3), showing standard deviations

Concentration and pcH ranges			ΔH_n	ΔH_{ion}
$10^2[L_T]$/M	$10^3[HL]$/M	pcH	kJ mol^{-1}	kJ mol^{-1}
4-Chlorocatechol				
3·000— 3·250	1·872— 2·091	7·319— 7·374	−27·83 ±0·40	28·68 ±0·40
4-Nitrocatechol				
0·650— 0·720	1·782— 1·889	6·228— 6·324	−32·51 ±0·18	23·98 ±0·18

Calorimetric Results for Copper Complex Formation.—Calorimetric results were obtained for the formation of 1 : 1 copper complexes alone since it was not possible to make similar determinations in the case of nickel because of interference by catalytic oxidation of the ligands. Heats of neutralisation of metal–ligand mixtures with potassium hydroxide were measured with use of an excess of ligand to prevent metal-ion hydrolysis, and it was arranged that the final ionic strength was 0·100M with respect to potassium nitrate; the proportions of metal, ligand, and added base were also adjusted so that only the 1 : 1 complex was formed [reaction (4)]. Corrections

$$H_2L + Cu^{2+} + 2OH^- \longrightarrow CuL + 2H_2O \qquad (4)$$

to the observed heats of reaction were made to allow for the heat of formation of water and heat of dilution of the added base. (The enthalpy change for the formation of water in 0·100M-KNO_3 at 25 °C has been determined.[6]) The correction for the heat of formation of water was calculated by determining the change in hydrogen-ion concentration during the reaction, and the amount of complex formed was determined from a knowledge of the metal–ligand stability constant, the ligand dissociation constant, and the final pcH value. The method of calculation is given in Part II.[1]

TABLE 4

Thermodynamic quantities for the first proton ionisation of catechol ligands in 0·100M-KNO_3 at 25 °C, showing standard deviation

Ligand	$-\log K_1^a$	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
Catechol	9·195 ±0·002	52·48 ±0·04	34·46 ±0·09	−60·26 ±0·42 *
4-Chlorocatechol	8·522 ±0·002	48·66 ±0·04	28·68 ±0·40	−66·94 ±1·26
4-Nitrocatechol	6·701 ±0·002	38·23 ±0·04	23·98 ±0·18	−48·11 ±0·84

* Part I.[6]

The enthalpy change for the neutralisation reaction, ΔH_n, was calculated from the heat of neutralisation and the concentration of 1 : 1 complex formed, [ML]. Results for a series of determinations are in Table 5.

TABLE 5

Calorimetric results for copper(II) complex formation with 4-chloro- and 4-nitro-catechol at 25 °C and ionic strength 0·100M (KNO_3), showing standard deviations

Concentration ranges			ΔH_n	ΔH^*
$10^3[M_T]$/M	$10^3[L_T]$/M	$10^4[ML]$/M	kJ mol^{-1}	kJ mol^{-1}
4-Chlorocatechol				
2·480— 6·442	6·190— 16·11	4·165— 9·295	−101·1 ± 0·3	11·93 ± 0·36
4-Nitrocatechol				
1·982— 2·973	4·870— 7·305	3·822— 9·282	−105·9 ± 0·2	7·15 ± 0·21

Using previously determined thermodynamic data[6] together with the values of ΔH_n, we calculated enthalpy changes for other equilibria. First, using the value of the enthalpy change for the formation of water in the same medium, from equation (4) we calculated the enthalpy change, ΔH^*, for the equilibrium (5), together with the

$$Cu^{2+} + H_2L \longrightarrow CuL + 2H^+ \qquad (5)$$

corresponding values of ΔG^* and ΔS^*.

Thermodynamic quantities for the ionisation of the ligands (Table 4) were also used to calculate corresponding thermodynamic values for equilibrium (6). Table 6

$$Cu^{2+} + HL^- \longrightarrow CuL + H^+ \qquad (6)$$

summarises the thermodynamic quantities for these equilibria and they are compared with corresponding values for the 1 : 1 copper–catechol complex reported in Part II.[1]

TABLE 6

Thermodynamic quantities for the formation of copper(II) complexes with catechols in 0·100M-KNO_3 at 25 °C showing standard deviations

Ligand	log K	$\frac{\Delta G}{\text{kJ mol}^{-1}}$	$\frac{\Delta H}{\text{kJ mol}^{-1}}$	$\frac{\Delta S}{\text{J K}^{-1}\text{ mol}^{-1}}$
(*a*) $Cu^{2+} + H_2L \longrightarrow CuL + 2H^+$				
Catechol	−8·345 ±0·009	47·66 ±0·04	13·39 ±0·80	−115 ± 2 *
4-Chlorocatechol	−7·602 ±0·011	43·40 ±0·04	11·93 ±0·36	−105 ± 1
4-Nitrocatechol	−5·888 ±0·010	33·60 ±0·04	7·15 ±0·21	−88·8 ± 0·4
(*b*) $Cu^{2+} + HL^- \longrightarrow CuL + H^+$				
Catechol	0·85 ±0·01	−4·85 ±0·04	−20·9 ±0·8	−54 ± 2 *
4-Chlorocatechol	0·92 ±0·01	−5·27 ±0·04	−16·7 ±0·8	−38 ± 2
4-Nitrocatechol	0·81 ±0·01	−4·64 ±0·04	−16·7 ±0·4	−42 ± 2

* Part II.[1]

Optical Studies.—In acidic aqueous solution the ligands catechol and 4-chlorocatechol are found to have high-intensity u.v. spectra with well defined peaks at 34 kK; no absorption occurs for these ligands in the region below 30 kK and hence the solutions are colourless. The ligand 4-nitrocatechol absorbs in the visible region and has a well defined peak at 28 kK.

The visible spectra of some 1 : 1 copper(II) complexes with substituted catechols are shown in Figure 1. In most cases the spectra have two important characteristics: (*a*) a typical broad asymmetric *d–d* band at 13·5 kK, of low intensity (spin-forbidden), characteristic of the spectra of copper(II) co-ordinated to four oxygen atoms, and (*b*) for most of the ligands shown, a high-intensity charge-transfer band whose peak varies between 22·5 kK for L-Dopa[3] to 26 kK for catechol, and whose position is clearly dependent upon the nature of the substituent. The copper(II)-4-nitrocatechol complex shows no charge-transfer band, but with 4-formylcatechol a shoulder at 22 kK suggests the presence of a charge-transfer band beneath the ligand absorption. Similar charge-transfer spectra were not observed in optical studies of the nickel complexes, which makes their instability in the presence of oxygen less readily explicable.

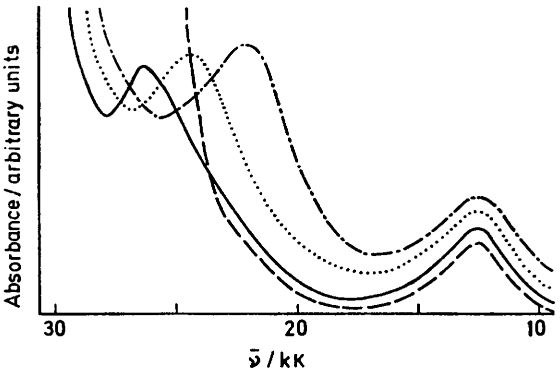

FIGURE 1 Spectra of copper(II) complexes of catechols: (——), catechol; (··········), 4-chlorocatechol; (— — —), 4-formylcatechol; (— · — · —), Dopa

DISCUSSION

The effect of substituent on ionisation of the ligands can be seen by considering the dissociation constants in Table 1. The pK (and hence ΔG_{ion}) decreases with increase in electron-withdrawing power of the substituent for both the first and second proton ionisation and therefore the acid strength decreases in the order of substituent $NO_2 > Cl > H$. The Born model of electrostatic solute–solvent interaction for weak acids in solution predicts a linear relationship between $\Delta G_{\text{ion}}^{\ominus}$ and $\Delta S_{\text{ion}}^{\ominus}$ for acids of a similar structure; the proportionality between these thermodynamic quantities

$$\Delta S_{\text{ion}}^{\ominus}/\Delta G_{\text{ion}}^{\ominus} = (\delta \ln D/\delta T)p \qquad (7)$$

may be shown to be (7), where D is the dielectric constant, T the absolute temperature, and p the pressure.[9]

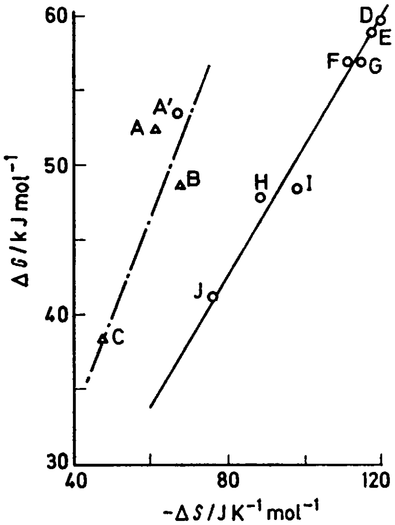

FIGURE 2 Plots of ΔG against ΔS for phenolic-type ionisations: circles and full line, *ortho*-substituted phenols with values at infinite dilution; triangles and broken line, 4-substituted catechols measured in 0·100M-KNO_3; A,A′ = catechol; B = 4-chlorocatechol; C = 4-nitrocatechol; D = *o*-propylphenol; E = *o*-methylphenol; F = *o*-methoxyphenol; G = phenol; H = *o*-formylphenol; I = *o*-chlorophenol; J = *o*-nitrophenol

Figure 2 shows a plot of $\Delta G_{\text{ion}}^{\ominus}$ against $\Delta S_{\text{ion}}^{\ominus}$ for the ionisation of *ortho*-substituted phenols[6] and a good linear relationship between these parameters is observed. The corresponding values of $\Delta G_{\text{ion}}^{\ominus}$ against $\Delta S_{\text{ion}}^{\ominus}$ for catechol (first proton ionisation, obtained by extrapolation to infinite dilution[6]) are plotted on the same diagram and it is seen that catechol, an *ortho*-substituted phenol, does not correlate with the other *ortho*-compounds. One explanation is that the structure

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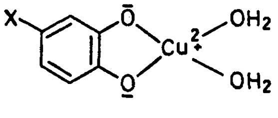
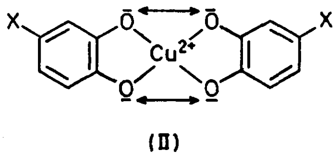
[9] E. J. King, 'Acid–Base Equilibria,' Pergamon Press, London, 1965.

of catechol in aqueous solution may be considerably different because of strong hydrogen bonding between adjacent hydroxyl groups.[6] There is, however, some correlation between the values of ΔG and ΔS obtained for the first proton ionisation of the catechol ligands in in 0·100M-KNO_3; this seems more plausible if one postulates a different structure for catechols in solution.

Table 2 shows that the stabilities of the copper(II) complexes for both the 1 : 1 and 2 : 1 species decrease with substituent in the order H > Cl > NO_2, and for the formation of the 1 : 1 nickel(II) complexes a similar trend is found. This is the order expected for complexes formed by simple σ-bonding between ligand and metal, *i.e.*, the acidity of the ligand increases with increase in electron-withdrawing power of the substituent and hence the base strength of the deprotonated ligand species is diminished. The Table also shows that for the addition of a second ligand anion to the 1 : 1 copper(II) complex of that anion, the log formation constant, log K_2^M, is generally between 2 and 3 units lower than log K_1^M. This may be understood by considering structures (I) and (II). The considerable increase in stability of formation of complex (I) over that of (II) is best explained in terms of the charge effects of the complex ions formed.[10] Thus in the formation of complex (II), coulombic repulsions between the negative oxygen atoms would tend to lower the stability, and an increase in the relative stability of this species with increase in electron-withdrawing power of the substituent would also be expected if the effect of the substituent is transmitted through the ligand such that the electron density on the catechol oxygens is lowered. This effect can be seen more clearly by examining the values of Δ (= log K_1^M – log K_2^M) given in Table 2. For formation of the nickel(II) complexes values of Δ do not fall uniformly, although the overall trend is similar to that of copper.



(I)



(II)

An examination of thermodynamic quantities for the formation of 1 : 1 copper(II) complexes (Table 6) shows that ΔH values for equilibrium (5) are positive and decrease with increasing acidity of the ligand (*i.e.*, ΔH = 13·39, 11·93, and 7·15 kJ mol^{-1} for substituents H, Cl, and NO_2 respectively). In general, for a series of substituted bidentate ligands of similar structure, the effects of removing two ligand protons and forming copper–ligand bonds would normally be expected to compensate each other as we move along the series (provided that enthalpies of hydration are constant and that the strength of bonding is determined by the basicity of the deprotonated ligand species alone) and hence ΔH for this process should remain relatively unaffected by changing substituent. In this case the values of ΔH indicate that for process (5) less energy is required as the ligand acidity increases. One possible explanation is that the bonding in the complexes is not simply due to coulombic attractions between species; however, since extensive hydrogen bonding is almost certainly present in these species,[6] solvation effects are expected to have a marked influence and this is the most likely explanation for the above effect; in other words it cannot be assumed that hydrational enthalpies are constant from ligand to ligand.

For equilibrium (6) values of ΔH are –20·9, –16·7, and –16·7 kJ mol^{-1} for substituents H, Cl, and NO_2 respectively and overall these results suggest that the effects of removing the second ligand proton and forming the 1 : 1 complex compensate each other more than in equilibrium (5). In this respect the second proton of the catechols appears to behave more like a simple phenolic proton, as suggested by the approximate value of the enthalpy change (ΔH = 21 kJ mol^{-1}) for the second proton ionisation of catechol determined in Part I.[6]

Values of ΔH for the first proton ionisation of the catechols (Table 4) indicate that the strength of binding of the proton decreases with increasing acidity of the ligand as measured by the pK_1^a value (*i.e.*, ΔH = 34·46, 28·68, and 23·98 kJ mol^{-1} for substituents H, Cl, and NO_2 respectively). The strength of binding of the second catechol proton (as measured by ΔH values for the ionisation) would also be expected to follow this order. Further, although it was not possible to determine such ΔH values, provided that the binding of the second proton does follow this order, then by use of the ΔH values for equilibrium (6) given in Table 6, together with arbitrary values of ΔH for the second proton ionisation, it can be shown that for the equilibrium (8)

$$Cu^{2+} + L^{2-} \longrightarrow CuL \qquad (8)$$

the strength of bonding in the 1 : 1 copper complexes, as measured by the ΔH value for this reaction, decreases in the order catechol > 4-chlorocatechol > 4-nitrocatechol. This indicates that the bonding present in these complexes is simple σ-bonding and that π-bonding by back-donation of *d*-electrons from copper to ligand is of little significance.

For oxidising metal ions and oxidisable ligands charge-transfer bands can be observed corresponding to transitions in which the metal ion is reduced. In general for charge transfer from ligand to metal the frequency is smaller the more oxidising the cation and the more reducing the ligand. In the case of the copper(II) catechol complexes the charge transfer is almost certainly from the ligand to the metal; this follows from the dependence of the frequency of the transition upon the nature of the substituent in the 4-position. Thus the energy of the band decreases in the order catechol, 4-chlorocatechol, L-Dopa and this

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[10] G. A. L'Heureux and A. E. Martell, *J. Inorg. Nuclear Chem.*, 1966, **28**, 481; this paper reports an inexplicably low value of pK_2^a for catechol (11·93).

is the same order as the increase in π-electron donating power of the 4-substituent. In the case of 4-nitrocatechol no charge-transfer band was detected and this is to be expected since the nitro-group is a strong electron-withdrawing substituent. Thus these results enable the catalytic oxidation of L-Dopa by molecular oxygen in the presence of iron(III) to be rationalised, although it has been found necessary to postulate a *two*-electron transfer in this case (probably as a rapid succession of two one electron-transfer steps) from the ligand to metal to oxygen.[11] This is probably partly due to the role of the O_2 molecule, however, since in the oxidation of ascorbic acid with copper(II) as catalyst, a similar overall two-electron change seems to demand the participation of *two* copper(II) ions on the basis of kinetic evidence.[12]

[2/1000 *Received, 4th May*, 1972]

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[11] R. F. Jameson, A. E. Martell, and (in part) J. E. Gorton, unpublished work.

[12] N. J. Blackburn and R. F. Jameson, unpublished work.