Characterization of Inner- and Outer-sphere Complexes by Thermodynamics and Absorption Spectra. Part 2.[1] Chloro-complexes of Copper(II)

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Evidence for inner-sphere $[CuCl]^+$ from charge-transfer and *d–d* spectra and from e.s.r. and thermodynamic data has been assessed. The extent of inner-sphere formation is *ca*. 30 and 55% in 2 mol dm^{-3} Na[ClO$_4$] and 4 mol dm^{-3} Li[ClO$_4$] respectively, from thermodynamic data. Formation constants for $[CuCl_n]^{2-n}$ (n = 1—4) for 25 °C and I = 5 mol dm^{-3} have been derived by spectrophotometry.

THE complex species formed between chloride ions and Cu^{II} at high ionic strength have been investigated as part of a project comprising the quantitative definition of the species in concentrated solutions encountered in hydrometallurgical processing. The advantages of identifying complexes as inner- or outer-sphere have been outlined for sulphate complexes of the first-row transition elements.[1]

Absorption spectra appear to provide a method of distinguishing between the two configurations, and Smithson and Williams [2] used the position of absorption bands for this purpose. The basis for the classification is that the weak low-energy bands of the aqua-ion that occur mainly in the visible spectrum arise from *d–d* transitions that are influenced by the close approach of ligands that occurs only in inner-sphere complexes. Conversely, in outer-sphere complexes the relatively long-range charge-transfer (c.t.) interactions between the ligand and the aqua-ion give rise to bands of higher energy in the u.v. and visible that may also have contributions from inner-sphere species.

Richards and Sykes [3] have shown that a complex-formation constant derived from absorption spectra is the sum of the constants of the individual configurations and is independent of wavelength. Hence the same value of the constant should be derived from *d–d* bands and from c.t. bands.

Three relevant investigations of the formation constants of the chloro-complexes of Cu^{II} at high ionic strength are those of Mironov *et al.*,[4] Khan and Schwing-Weill,[5] and Bjerrum and Skibsted.[6] Mironov *et al.* investigated only the monochloro-complex and observed a dependence of the value of the formation constant on wavelength. They apparently derived the inner-sphere constant from *d–d* spectra and the sum of the inner- and outer-sphere constants from c.t. spectra. These findings require explanation. The constants from the other two investigations showed very poor agreement (Table 1).

TABLE 1

Recent literature values for the chloro-complexes of copper(II) in 5 mol dm^{-3} sodium perchlorate

K_1 /dm^3 mol^{-1}	β_2 /dm^6 mol^{-2}	β_3 /dm^9 mol^{-3}	β_4 /dm^{12} mol^{-4}	ε_1 (250 nm)/dm^3 mol^{-1} cm^{-1}	Ref.
1.5	0.63	0.088	0.003 2	2 705	6
4.0	4.8	2.0	0.24	1 042	5

Bjerrum and Skibsted [6] combined spectra with an activity expression for chloride ions to derive the formation constants, whereas Khan and Schwing-Weill [5] processed absorbance measurements by a least-squares method. Bjerrum and Skibsted interpreted the results of Khan and Schwing-Weill to calculate the absorption coefficients of the chloro-complexes containing one, two, and three ligands.

The objects of this investigation are to assess the extent of inner-sphere formation in the monochloro-complex of Cu^{II} from published data, and to explain the dependence of the formation constant on wavelength reported by Mironov *et al.*[4] The derivation of the formation constants of all the chloro-complexes was necessary for this purpose.

RESULTS

In order to assess the results of Mironov *et al.*,[4] K_1 for $[CuCl]^+$ must be derived from c.t. and *d–d* bands in the absence of the higher complexes. Conditions for their absence could be established by deriving their formation constants from u.v. spectra.

The Copper(II)*–Chloride System: U.v. Spectra.*—The effect of chloride-ion concentration on the u.v. spectrum of 0.002 75 mol dm^{-3} Cu[ClO$_4$]$_2$ revealed the emergence of a new band with a peak at 248 nm at a concentration of 0.2 mol dm^{-3} (Figure 1). There was little change in the peak position as the concentration increased from 0.2 to 0.8 mol

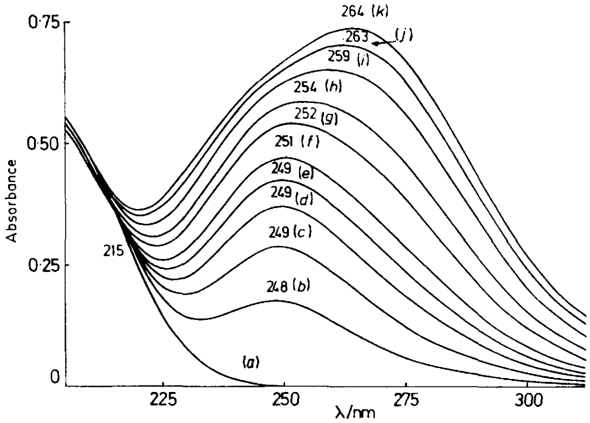

FIGURE 1 Effect of chloride concentration on the absorption spectrum of 0.002 75 mol dm^{-3} Cu[ClO$_4$]$_2$ at 25 °C and I = 5 mol dm^{-3} in 1-mm cells. [Cl$^-$] = 0 (*a*), 0.2 (*b*), 0.4 (*c*), 0.6 (*d*), 0.8 (*e*), 1.0 (*f*), 1.5 (*g*), 2.0 (*h*), 3.0 (*i*), 4.0 (*j*), and 4.89 mol dm^{-3} (*k*)

TABLE 2

Values of $\beta_n[(\mathrm{dm^3\,mol^{-1}})^n]$ and ε_n ($\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) for $[\mathrm{CuCl}_n]^{2-n}$ derived from u.v. spectra for I = 5 mol dm^{-3}

	[Cu$^{\mathrm{II}}$]	[Cl$^-$]		ε_n		
n	mol dm^{-3}		β_n	250 nm	280 nm	Ref.
1	0.016—0.101	0.03	1.43 ± 0.09	2 710 ± 10	550 ± 5	This work
1			1.5	2 705 ± 10	563 ± 2	6
1	0.005 8	0.07—0.5	1.03 ± 0.08	3 600 ± 34		This work
2	0.004 53	1.2—2.2	0.58 ± 0.03	2 020 ± 40	3 230 ± 20	This work
2			0.63	2 002 ± 34	3 150 ± 23	6
3	0.004 53	2.5—4.0	0.011 ± 0.002	4 260 ± 350	670 ± 240	This work
			0.088	2 810 ± 71	1 636 ± 60	6

dm^{-3}, indicating that only the first complex predominates for these conditions. An isosbestic point at 215 nm is consistent with two absorbing species, the copper(II) aqua-ion and the monochloro-complex. The latter could be present as inner- and outer-sphere species, but, if so, the constant ratio of their concentrations ensures that the sum of their absorbances will be equivalent to the absorbance of a single species with regard to the interpretation of the isosbestic point. The progressive peak shift as the concentration of chloride was increased from 0.8 to 5.0 mol dm^{-3} indicated increasing formation of the higher complexes, as also evidenced by the absence of an isosbestic point under these conditions.

For the determination of K_1, the chloride concentration was restricted to a low value (0.03 mol dm^{-3}) to reduce the possibility of the formation of higher complexes. By recording differential spectra with chloride-free copper as the reference solution, the spectra of increasing concentrations of the monochloro-complex appeared as the copper(II) concentration was increased at a constant concentration of chloride (Figure 2). The results were processed by the spectrophotometric variation of the LETAGROP computer program, SPEFO.[7] Values for K_1 and the absorption coefficients were derived and agree well with those of Bjerrum and Skibsted [6] (Table 2).

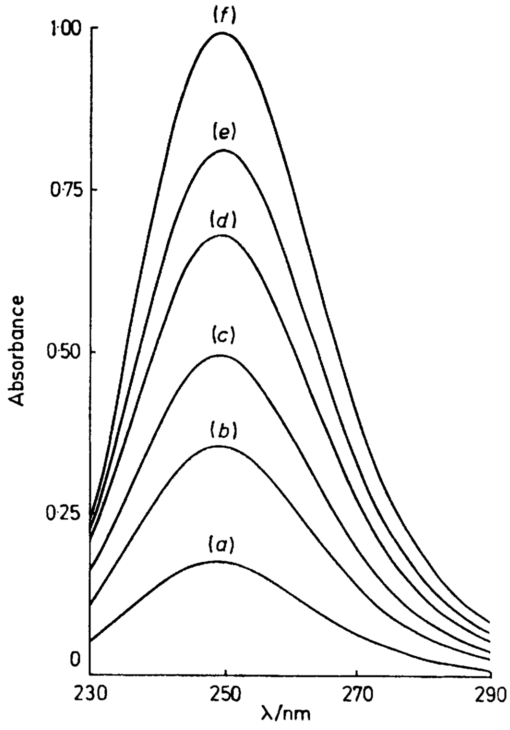

FIGURE 2 Absorption spectra of 0.03 mol dm^{-3} NaCl containing Cu[ClO$_4$]$_2$ at 25 °C and I = 5 mol dm^{-3} in 1-mm cells with chloride-free references. [Cu$^{\mathrm{II}}$] = 0.016 8 (*a*), 0.033 6 (*b*), 0.047 (*c*), 0.067 2 (*d*), 0.080 6 (*e*), and 0.101 mol dm^{-3} (*f*)

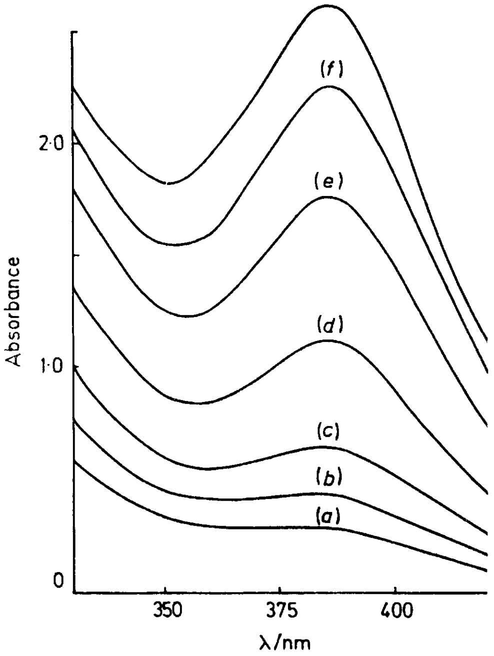

FIGURE 3 Effect of high concentrations of chloride ions on the absorption spectrum of 0.017 4 mol dm^{-3} Cu[ClO$_4$]$_2$ in 1-mm cells. [Cl$^-$] = 5.0 (*a*), 5.5 (*b*), 6.0 (*c*), 7.0 (*d*), 8.0 (*e*), 9.0 (*f*), and 10.0 mol dm^{-3} (*g*)

Introduction of K_2 to the program input resulted in the values $K_1 = 2.35 \pm 2.18$ and $K_2 = 5.22 \pm 5.03$ dm^3 mol^{-1}, a clear indication of a very poor fit. Thus the two different approaches of the present work and that of Bjerrum and Skibsted [6] pointed to the same conclusion: that K_1 and ε_1 could be well defined and that only the first complex, [CuCl]$^+$, was present for [Cl$^-$] up to 0.03 mol dm^{-3}. It was now possible to introduce the known values for K_1 and ε_1 from 250 to 280 nm, together with absorbance values for a range of solutions containing substantially [CuCl]$^+$ and CuCl$_2$, into the SPEFO program. A suitable range of ligand concentrations was 1.2—2.2 mol dm^{-3}, chosen from the species distribution calculated from the constants of Bjerrum and Skibsted.[6] In this region, the proportion of [CuCl]$^+$ and CuCl$_2$ changed from 47 to 39%, and from 24 to 37%, respectively. The resulting β_2 and ε_2 values were well defined (Table 2) and agreed well with those of Bjerrum and Skibsted.[6]

The constants for [CuCl$_3$]$^-$ were derived by repeating the process using absorbance values of solutions containing only the first three complex species. From the species distribution, values of ligand concentration from 2.5 to 4.0 mol dm^{-3} appeared to be suitable. The resulting values of β_3 and ε_3 agreed poorly with those of Bjerrum and Skibsted,[6] and were less well defined than corresponding values for the lower complexes (Table 2). This situation probably reflects smaller differences between the spectra of the second and third complexes compared with those between the spectra of the first and second.

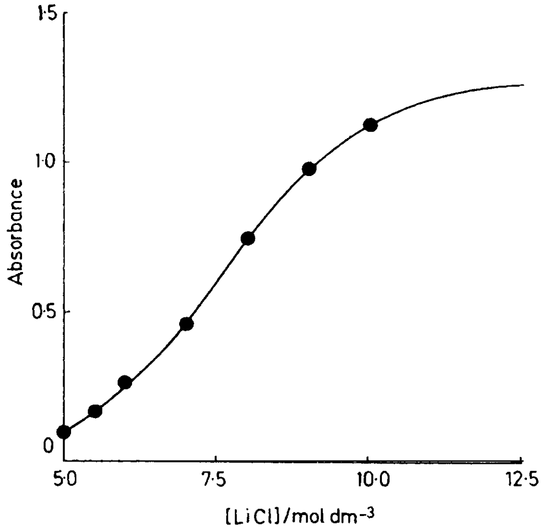

FIGURE 4 Variation of the absorbance of 0.017 4 mol dm^{-3} $Cu[ClO_4]_2$ at 420 nm with concentration of LiCl in 1-mm cells

A value of β_4 was derived from a new absorption band appearing in the region of 390 nm at high concentrations of lithium chloride of 5—10 mol dm^{-3} (Figure 3). If this new band is due to the formation of $[CuCl_4]^{2-}$, as assumed by Bjerrum and Skibsted,[6] then provided that it is possible to raise the ligand concentration sufficiently to cause practically all the copper(II) to exist in this form, a plot of absorbance against ligand concentration should approach a limiting value from which ε for $[CuCl_4]^{2-}$ could be derived (Figure 4). A short extrapolation of ligand concentration from 10 to 12 mol dm^{-3} gave ε_4 (420 nm) *ca.* 730 dm^3 mol^{-1} cm^{-1}. From absorbance values at 420 nm of solutions of I = 5 mol dm^{-3} containing 3.0, 4.2, and 5.0 mol dm^{-3} NaCl, the concentrations of $[CuCl_4]^{2-}$ were calculated and β_4 values derived from equation (1) using K_1, β_2, and β_3

$$\alpha_4 = \beta_4[Cl^-]^4 / \left(1 + \sum_{n=1}^{n=4} \beta_n [Cl^-]^n\right) \quad (1)$$

values already derived either from this work or by Bjerrum and Skibsted[6] (Table 3). The former set of constants yielded a β_4 value that compared well with that of Bjerrum and Skibsted, whereas the latter set gave less consistent values.

TABLE 3

Values of β_4 for $[CuCl_4]^{2-}$ at I = 5 mol dm^{-3}

[Cu^{II}]	[Cl$^-$]			β_4/dm^{12} mol^{-4}	
mol dm^{-3}		A(420 nm)	α_4	*a*	*b*
0.027 5	3.0	0.515	0.025 6	0.003 58	0.004 41
0.027 5	4.2	0.775	0.038 6	0.002 46	0.003 22
0.017 4	5.0	1.09	0.085 6	0.003 65	0.005 28

[a] Using β_1—β_3 from this work. [b] Using β_1—β_3 from ref. 6 (β_4 = 0.003 2 dm^{12} mol^{-4}).

The validity of the formation constants derived by Bjerrum and Skibsted[6] has been confirmed and the corresponding distribution of species could be used to indicate the range of ligand concentrations suitable for ensuring the absence of complex species containing more than one chloride ion. Hence the derivation of K_1 from visible spectra could proceed.

The Copper(II)*-Chloride System: Visible Spectra.*—Species-distribution calculations showed that α_1 = 0.23 and α_2 = 0.02 for a ligand concentration of 0.2 mol dm^{-3}. Spectra recorded with ligand concentrations of 0.1 (Figure 5), 0.2, and 0.07—0.5 mol dm^{-3} were processed by the SPEFO program (Table 4).

There was good agreement between values for K_1 and ε_1 for constant ligand concentrations of 0.1 and 0.2 mol dm^{-3} when $\alpha_2 \leqslant 0.02$, but when α_2 increased to 0.08, K_1 decreased sharply and ε_1 showed a large increase.

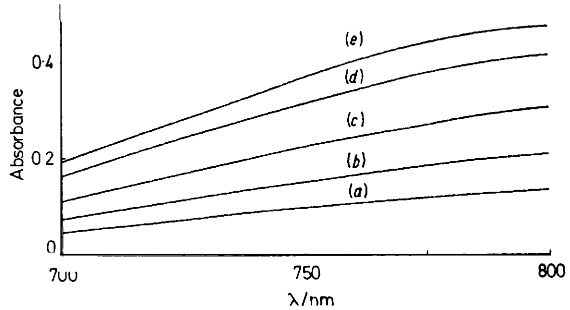

FIGURE 5 Absorption spectra of 0.1 mol dm^{-3} NaCl containing $Cu[ClO_4]_2$ at 25 °C and I = 5 mol dm^{-3} in 1-cm cells with chloride-free references. [Cu^{II}] = 0.050 (*a*), 0.084 (*b*), 0.126 (*c*), 0.203 (*d*), and 0.232 mol dm^{-3} (*e*)

DISCUSSION

The formation constants for the chloro-complexes of Cu^{II} for an ionic strength I of 5.0 mol dm^{-3} measured here were generally in good agreement with those derived by Bjerrum and Skibsted[6] but differed markedly from those given by Khan and Schwing-Weill[5] (Tables 1 and 2). Although all three sets of constants were derived from spectrophotometric measurements, the results were interpreted by different methods. It is significant that Bjerrum and Skibsted derived their constants by incor-

TABLE 4

Values for K_1 and ε_1 for $[CuCl]^+$ derived from visible spectra for I = 5 mol dm^{-3}

[Cu^{II}]	[Cl$^-$]		ε_1/dm^3 mol^{-1} cm^{-1}		K_1
mol dm^{-3}		α_2	730 nm	790 nm	dm^3 mol^{-1}
0.050 4—0.232	0.1	0.1	21.4 ± 0.1	31.5 ± 0.2	1.42 ± 0.01
0.042—0.437	0.2	0.02	21.8 ± 0.1	32.3 ± 0.1	1.24 ± 0.09
0.072 5	0.07—0.5	0—0.08	* 37.2 ± 0.2	* 59.5 ± 0.2	* 0.52 ± 0.03

* Average value for the range of ligand concentrations.

porating their measurements with some of those of Khan and Schwing-Weill.

For a suitable range of ligand concentrations, there was good agreement between K_1 derived from c.t. and *d–d* spectra (Tables 2 and 4), as expected from the assertion by Richards and Sykes[3] that only the sum of $K_1^{\text{in.}}$ and $K_1^{\text{out.}}$ can be so obtained. By contrast, Mironov *et al.*[4] suggested that they had derived $K_1 = 0.87$ from c.t. spectra and $K_1^{\text{in.}} = 0.45$ dm^3 mol^{-1} from *d–d* bands for $I = 3$ mol dm^{-3} maintained by lithium perchlorate with concentrations of ligand up to 3.0 mol dm^{-3}. At this ligand concentration, substantial amounts of complexes containing more than one ligand would be expected and their concentrations could be calculated from the formation constants for the appropriate medium. Since the constants were not available, approximate values were derived. For this purpose, it was noted that the variations of K_1 for $[\text{FeCl}]^{2+}$ in 1.0—5.0 mol dm^{-3} solutions of perchloric acid and perchloric acid mixtures with sodium perchlorate have been closely predicted from the single value in 5 mol dm^{-3} HClO_4 by a method based on changes in activities.[8] Thus for the Cu^{II}–Cl system equation (2) is derived, where $K_{1\text{t}}^{\text{in.}}$ and $K_1^{\text{in.}}$ refer to the thermodynamic constant and the conditional constant (molar concentration units) respectively, and a and y are the corresponding activities and activity coefficients. For solutions of high ionic strength, Bjerrum[9] introduced the approximation that $y_3/y_1 = C$ (constant) in a specified medium on the basis that the activity coefficients depend on chemical structure rather than charge. Similar equations apply for the stepwise constants K_2, K_3, and K_4, and the ratio of the corresponding molar activity coefficients is also C. Since $C_n \approx C_{n+1}$, we obtain equation (3) where y, y' and

$$\underset{1}{[\text{Cu(OH}_2)_6]^{2+}} + \underset{2}{\text{Cl}^-} \longrightarrow \underset{3}{[\text{Cu(OH}_2)_5\text{Cl}]^+} + \text{H}_2\text{O}$$

$$K_{1\text{t}}^{\text{in.}} = \frac{a_3 a_{\text{H}_2\text{O}}}{a_1 a_2} = K_1^{\text{in.}} \frac{y_3}{y_1 y_2} \cdot a_{\text{H}_2\text{O}} \qquad (2)$$

$$K_n(3 \text{ mol dm}^{-3}) = K_n(5 \text{ mol dm}^{-3})(y \,.\, a'_{\text{H}_2\text{O}}/y' \,.\, a_{\text{H}_2\text{O}}) \qquad (3)$$

$a_{\text{H}_2\text{O}}$, $a'_{\text{H}_2\text{O}}$ refer to solutions of $I = 3$ and 5 mol dm^{-3}, respectively. Since the activity coefficients of chloride ions in $\text{Na[ClO}_4]$ solutions are not available, use was made of the Guggenheim assumption employed by Heistand and Clearfield[8] that $y_{\text{Cl}} \cong y\pm_{\text{HCl}}$ and Harned's rule (see ref. 10) regarding activity coefficients of mixed electrolytes. The latter has been shown to apply to the HCl–$\text{Na[ClO}_4]$ system up to $I = 1$ mol dm^{-3}.[11] Extrapolation of the resulting equation (4) (where $\gamma\pm_{\text{HCl}}$

$$\log\gamma\pm_{\text{HCl}} = \log\gamma\pm_{\text{HCl(0)}} - 0.024\,4m \qquad (4)$$

and $\gamma\pm_{\text{HCl(0)}}$ are the mean molal activity coefficients for a total electrolyte molality m and m molal HCl respectively), from solution concentrations of 1 to 5 mol dm^{-3}, allowed predictions of K_1 for $[\text{FeCl}]^{2+}$ that agreed well with experimental values.[8] Values for use in the Cu^{II}–Cl^- system were derived from data shown in Table 5. The mean molal activity coefficients were converted into mean molar values[10] from the densities of sodium perchlorate solutions;[12] $a_{\text{H}_2\text{O}}$ was taken from ref. 13. Hence $K_n^{\text{in.}}(3 \text{ mol dm}^{-3}) = K_n^{\text{in.}}(5 \text{ mol dm}^{-3}) \times 0.347$. Values for K_1, β_2, β_3, and β_4 were 0.52 dm^3 mol^{-1}, 0.078 dm^6 mol^{-2}, 0.003 8 dm^9 mol^{-3}, and 4.6×10^{-5} dm^{12} mol^{-4} in 3 mol dm^{-3} $\text{Na[ClO}_4]$. The corresponding distribution of species (Table 6) shows that, at ligand concentrations of 2 and 3 mol dm^{-3}, CuCl_2 is present in significant proportions. The formation constants would be larger by only *ca.* 15% if $[\text{CuCl}]^+$ were assumed to be entirely outer sphere, because the $a_{\text{H}_2\text{O}}$ term would be omitted from the calculation for K_1.

TABLE 5

Derivation of $y\pm_{\text{HCl}}$, and values for $a_{\text{H}_2\text{O}}$[13]

$\text{Na[ClO}_4]$					
c/mol dm^{-3}	m/mol kg^{-1}	$\gamma\pm_{\text{HCl(0)}}$	$\gamma\pm_{\text{HCl}}$	$y\pm_{\text{HCl}}$	$a_{\text{H}_2\text{O}}$
3	3.50	1.50	1.23	1.44	0.884
5	6.63	3.96	2.73	3.62	0.772

TABLE 6

Distribution of species in the Cu^{II}–Cl^- system in 3 mol dm^{-3} $\text{Na[ClO}_4]$

No. of Cl^-	α_1	α_2	α_3	α_4
1	0.33	0.049	0.002	0
2	0.44	0.131	0.013	0
3	0.46	0.210	0.030	0

Hence it appears that the failure of Mironov *et al.*[4] to take account of species containing more than one ligand resulted in the derivation of a K_1 value from u.v. spectra that was higher than that derived from visible spectra. The incorrect assignment of the formation constants of the outer- and inner-sphere species followed. A similar effect was observed in this work for a medium of 5 mol dm^{-3} $\text{Na[ClO}_4]$ for a range of ligand concentrations from 0.07 to 0.5 mol dm^{-3} with K_1 values from u.v. spectra and visible spectra of 1.03 (Table 2) and 0.52 dm^3 mol^{-1} (Table 4), respectively. High values of ε_1 were derived in both regions of the spectrum (Table 4).

Although the extent of inner-sphere formation of $[\text{CuCl}]^+$ cannot be gauged from the absorption spectra, the presence of some inner-sphere species is indicated by the modification of the visible spectrum of the copper(II) aqua-ion by chloride ions.

Thermodynamic values are more useful. The enthalpy and entropy of formation of a complex species involving hard acceptors and hard donors reflect the extent of inner-sphere character because they are largely a result of solvation changes and hence are almost independent of the particular metal ion, especially for an isovalent series with the same ligand.[14] The formation of inner-sphere complexes involves the displacement of water molecules so that values of $\Delta H^\ominus$ and $T\Delta S^\ominus$ at infinite dilution are higher by about 20 and 25 kJ mol^{-1}, respectively, at 25 °C than the corresponding values for the outer-sphere species. At high ionic strength (5 mol dm^{-3}), $\Delta H^\ominus$ and $T\Delta S^\ominus$ were reduced by 5—9 and 15—20 kJ mol^{-1}, respectively, for the formation of both inner- and outer-sphere sulphato-complexes of the first-row transition elements.[1] Hence the differential values showed little change.

Few thermodynamic measurements for the weak labile chloride complexes of bivalent metal ions are available because of experimental difficulties. However, the inner- and outer-sphere monochloro-complexes of Cr^{III} could be distinguished because of the inert character of the inner-sphere complex. Inner-sphere species [15] were found to have values for $\Delta H^{\ominus}$ and $T\Delta S^{\ominus}$ that were respectively about 20 and 25 kJ mol^{-1} higher than their outer-sphere counterparts [16] at $I = 1.0$ mol dm^{-3}. Comparison of $\Delta H^{\ominus}$ for the monochloro-complexes of Cu^{II} and Cr^{III} should indicate the extent of inner-sphere formation, since values for $\Delta H^{\ominus}$ of *ca.* 0 and *ca.* 24 kJ mol^{-1} correspond to $\alpha_1^{\text{in.}}$ of 0 and 1, respectively (Table 7).

TABLE 7

Thermodynamic values (kJ mol^{-1}) for monochloro-complexes at 25 °C

Metal ion	$\frac{I}{\text{mol dm}^{-3}}$	Class [a]	$\Delta H^{\ominus}$	$T\Delta S^{\ominus}$	Ref.
Cr^{3+}	1.0	o.s.	−1.7	−2.5	16
	0.98	i.s.	25.1	19.7	15
	4.0	i.s.	23.4	19.7	15
Cu^{2+}	2.0		6.6	7.1	*b*
	4.0		13.5	13.3	17

[a] o.s. = Outer sphere, i.s. = inner sphere. [b] M. B. Kennedy and M. W. Lister, *Canad. J. Chem.*, 1966, **44**, 1709.

Values of $\Delta H^{\ominus}$ for $[CuCl]^+$ were available for $I = 2.0$ and 4.0 mol dm^{-3} (sodium and lithium perchlorate, respectively) and by comparison with those for $[CrCl]^{2+}$ over the same range of ionic strength, approximate values for $\alpha_1^{\text{in.}}$ were $\Delta H^{\ominus}/24$ (Table 7). On this basis, $\alpha_1^{\text{in.}}$ increases from 0.28 in 2 mol dm^{-3} $Na[ClO_4]$ to 0.56 in 4 mol dm^{-3} $Li[ClO_4]$: an increase would be expected on the grounds of a decrease in a_{H_2O} for these media from 0.93 to 0.73, respectively.[13] An approximation of the expected increase can be gained from equations for $K_{1t}^{\text{out.}}$ analogous to those for $K_{1t}^{\text{in.}}$. It can be shown that equation (5) is applicable, where I_1 and I_2

$$\frac{(K_1^{\text{in.}}/K_1^{\text{out.}})_{I_1}}{(K_1^{\text{in.}}/K_1^{\text{out.}})_{I_2}} = \frac{(a_{H_2O})_{I_2}}{(a_{H_2O})_{I_1}} = \frac{0.93}{0.73} = 1.27 \qquad (5)$$

refer to values of the ionic strength of two solutions, by assuming that the ratio of the activity coefficients of $[Cu(OH_2)_5Cl]^+$ and $[Cu(OH_2)_6Cl]^+$ in the same solution is close to 1 : 1. Since $\alpha_1^{\text{in.}}$ is given by expression (6),

$$\alpha_1^{\text{in.}} = \frac{K_1^{\text{in.}}}{K_1^{\text{in.}} + K_1^{\text{out.}}} = \frac{K_1^{\text{in.}}/K_1^{\text{out.}}}{(K_1^{\text{in.}}/K_1^{\text{out.}}) + 1} \qquad (6)$$

then if $\alpha_1^{\text{in.}} = 0.28$, $K_1^{\text{in.}}/K_1^{\text{out.}} = 0.39$ in 2 mol dm^{-3} $Na[ClO_4]$. From the change of a_{H_2O} in 4 mol dm^{-3} $Li[ClO_4]$, $K_1^{\text{in.}}/K_1^{\text{out.}}$ becomes $0.39 \times 1.27 = 0.50$, and $\alpha_1^{\text{in.}}$ becomes 0.33. Hence, an increase of $\Delta H^{\ominus}$ to 7.9 kJ mol^{-1} in 4 mol dm^{-3} $Li[ClO_4]$ would be expected, in poor agreement with the published value of 13.5 kJ mol^{-1} (Table 7). Further $\Delta H^{\ominus}$ values for $[CuCl]^+$ are required in order to assess the accuracy of the two sets of published results.

Other evidence for the presence of inner-sphere structure in $[CuCl]^+$ emerged from e.s.r. measurements of the chloride–, bromide–, and sulphate–copper(II) systems in 2 mol dm^{-3} $Li[ClO_4]$.[17] Constant *g* factors for increasing concentrations of ligand from 0 to 2 mol dm^{-3} in the bromide and sulphate systems indicated the absence of inner-sphere species, since variations in the *g* factor reflect changes in the immediate environment of the metal ion. Other evidence for the predominance of outer-sphere $[CuBr]^+$ and $Cu[SO_4]$ was the slight change in the *d–d* spectrum of the copper(II) aqua-ion compared with the large increase in the c.t. band produced by high ligand concentrations in 2 mol dm^{-3} $Li[ClO_4]$.[17] Thermodynamic values for the $Cu[SO_4]$ complex support the outer-sphere character, especially at high ionic strength: thus, $\Delta H^{\ominus}$ and $T\Delta S^{\ominus}$ were about 0 and 3.6 kJ mol^{-1} respectively for an ionic medium of 5 mol dm^{-3}.[1] By contrast, the *g* factor for the copper(II) ion decreased with increasing concentration of chloride ions. Although the formation of at least one inner-sphere complex was indicated, this evidence regarding the structure of $[CuCl]^+$ is meaningful only if the formation of the inner-sphere $CuCl_2$ is insignificant and hence does not contribute to the decrease of the *g* factor. An indication of the likelihood of such an event was made by calculating the formation constants and the species distribution for a medium of 2 mol dm^{-3} $Na[ClO_4]$. The method outlined above was employed, with the result that $K_n(2 \text{ mol dm}^{-3}) = K_n(5 \text{ mol dm}^{-3}) \times 0.24$. From the corresponding species distribution, α_1 and α_2 were 0.38 and 0.08 respectively for the highest chloride-ion concentration of 2 mol dm^{-3}. Thus, it appeared that the decrease in the *g* factor was indeed related to the formation of inner-sphere $[CuCl]^+$, but that no estimate of the extent of formation could be made.

It was concluded that although there was strong qualitative evidence for some inner-sphere character of $[CuCl]^+$ from *d–d* spectra, e.s.r. measurements, and thermodynamics, only the last method could be used for a semi-quantitative assessment of α_1 of 0.28 and 0.56 in 2 mol dm^{-3} $Na[ClO_4]$ and 4 mol dm^{-3} $Li[ClO_4]$, respectively.

EXPERIMENTAL

AnalaR-grade materials were used. A stock solution of copper(II) perchlorate was prepared by the addition of a slight excess of sodium hydroxide solution to a solution of the trihydrate salt of copper(II) nitrate for quantitative precipitation of $Cu[OH]_2$. After thorough washing with water, the precipitate was dissolved in a slight excess of perchloric acid. The copper(II) concentration was determined by standard thiosulphate, and the perchloric acid concentration by acid titration of the filtrate following precipitation of $Cu[OH]_2$ by a measured excess of standard sodium hydroxide solution. An ionic strength of 5 mol dm^{-3} was maintained by $Na[ClO_4]$; 0.1 mol dm^{-3} $HClO_4$ prevented hydrolysis of Cu^{II}.

Spectra were recorded on a Beckman ACTA III spectrophotometer fitted with temperature-controlled cell holders suitable for cells having pathlengths of 0.1—1.0 cm. Absorbance readings from the digital display of the instrument were taken at intervals of 5 nm for use in the calculations.

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