Entropy Contribution to the Relative Solution Stability of Copper(III) and Nickel(III) Tetraazamacrocyclic Complexes in Aqueous Perchloric Acid

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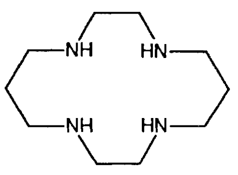
Solutions containing equimolecular amounts of $[Ni^{II}(cyclam)][ClO_4]_2$ and $[Cu^{II}(cyclam)][ClO_4]_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) of varying concentration of $HClO_4$ (4–11.56 mol dm^{-3}) were investigated through voltammetric techniques and the potentials associated with the Ni^{II}–Ni^{III} and Cu^{II}–Cu^{III} redox changes determined. The potential difference, $E_{Cu} - E_{Ni}$, which is related to the metathetic equilibrium $[Cu^{III}L]^{3+} + [Ni^{II}L]^{2+} \rightleftharpoons [Cu^{II}L]^{2+} + [Ni^{III}L]^{3+}$, becomes less positive with increasing $HClO_4$ concentration, indicating a stabilizing effect on the copper(III) complex, compared to Ni^{III}. This effect is related to the competition by the ions of the electrolyte for the water molecules co-ordinated to the electroactive species. The entropy change ΔS° associated with the metathetic equilibrium was determined through voltammetric investigations performed at varying temperatures (−15 to +40 °C). On the basis of ΔS° values, it is suggested that, below an $HClO_4$ concentration of 8 mol dm^{-3}, water molecules occupy the available co-ordination sites in the electroactive metal complexes; at a higher concentration the solvent molecules are replaced by ClO_4^- anions.

Encircling of a 3d divalent metal ion by a 14-membered tetraaza macrocycle, *e.g.* cyclam (1,4,8,11,tetraazacyclotetradecane), makes available high and otherwise hardly accessible oxidation states: in particular, trivalent nickel and copper.[1] Essentially due to the considerably larger value of its third ionization potential, the relative solution stability of the $[Cu^{III}(cyclam)]^{3+}$ complex is much lower than that of the corresponding trivalent nickel species. The complex $[Ni^{III}(cyclam)]^{3+}$ is fairly stable in non-aqueous solvents, indefinitely stable in aqueous acidic solution and can also be isolated as a crystalline solid;[2–4] on the other hand, $[Cu^{III}(cyclam)]^{3+}$ is stable in solution on the time-scale of cyclic voltammetry in strictly anhydrous acetonitrile;[5] also in water but only if the solution is strongly acidic.[6] The discovery of the stabilizing effect exerted by acidity on trivalent copper was derived from Barefield's observations[7] that ligand oxidation by a trivalent metal centre and subsequent decomposition of the complex is promoted by bases (including water). In particular, the addition of strong acid quenches or makes slower the rate-determining step of the base-promoted decomposition process and allows the strongly oxidizing complex, *e.g.* $[Cu(cyclam)]^{3+}$, to persist in solution.

In this work we wished to ascertain whether the acidity of the solution could affect the relative stability of trivalent nickel and copper cyclam complexes not only from a *kinetic* point of view, but also from a *thermodynamic* one. To do that we investigated through voltammetric techniques solutions containing either $[Ni^{II}(cyclam)][ClO_4]_2$ and $[Cu^{II}(cyclam)][ClO_4]_2$ over the $HClO_4$ concentration range 4.0–11.6 mol dm^{-3}. Electrochemical studies were performed at varying temperatures, using an isothermal cell assembly, to determine the entropy change.

Experimental

1,4,8,11-Tetraazacyclotetradecane[8] (cyclam) and *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane[9] were synthesised following the literature methods. The $M^{II}L(ClO_4)_2$ complexes were obtained through reaction of the metal perchlorate and the ligand in boiling ethanol and were recrystallized from methanol. Perchloric acid solutions were prepared by diluting 70% $HClO_4$ (Fluka).



cyclam

Voltammetric investigations were carried out on a P.A.R. model 273 potentiostat/galvanostat, driven by an IBM AT personal computer, through dedicated software. A conventional three-electrode cell was employed, which was thermostatted through circulating water. The working electrode was a platinum microsphere, which, before each measurement, was treated by dipping in boiling concentrated nitric acid and through precyclization at high-potential scan rate, over the available window of potential. A silver wire was used as a pseudo-reference electrode and a platinum coil acted as an auxiliary electrode.

Results and Discussion

In a typical experiment, equimolar amounts of $[Ni^{II}(cyclam)][ClO_4]_2$ and $[Cu^{II}(cyclam)][ClO_4]_2$ complexes (*e.g.* 10^{-3} mol dm^{-3}) were dissolved in aqueous perchloric acid of a given concentration and the solution was investigated through the differential pulse voltammetry (DPV) technique, using a three-electrode cell assembly. The DPV profile showed two regular peaks, with a half-peak width of about 90 mV, in each case. An half-peak width of 90.4 mV is expected for a reversible one-electron process, at 25 °C.[10] The less anodic peak was ascribed to the one-electron oxidation of the nickel(II) complex, the more anodic peak to that of the copper(II) complex. In view of the lack of a reliable standard reference electrode in concentrated perchloric acid, we simply looked at the separation of the two peaks, $\Delta E = E_{\frac{1}{2}}(Cu^{III}\text{–}Cu^{II}) - E_{\frac{1}{2}}(Ni^{III}\text{–}Ni^{II})$. This quantity is related to the oxidation and reduction equilibrium (1). In particular, ΔE is related to the equilibrium constant for equation (1) through equation (2). Thus, the larger ΔE, the

$$[Cu^{III}L]^{3+} + [Ni^{II}L]^{2+} \xrightleftharpoons{K} [Cu^{II}L]^{2+} + [Ni^{III}L]^{3+} \qquad (1)$$

$$\ln K = \Delta E(F/RT) \qquad (2)$$

greater is the stability of the trivalent nickel complex compared to the trivalent copper analogue.

The solution of lowest acidity we considered was 4.0 mol dm^{-3} $HClO_4$. At a lower concentration of acid, the Cu^{II}–Cu^{III} oxidation process did not exhibit fully reversible behaviour [as shown, in particular, by the cyclic voltammetry (CV) response, where the cathodic current was significantly less than the anodic one]. This indicates that the $[Cu^{III}(cyclam)]^{3+}$ complex is stable on the time-scale of the voltammetry experiment, performed at moderate potential scan rate, only at an $HClO_4$ concentration $\geqslant 4$ mol dm^{-3}. At this acid concentration, ΔE = 320 mV and $\log K = 5.4$, *i.e.* the formation of the $[Ni^{III}L]^{3+}$ complex is substantially more favoured compared to the formation of the $[Cu^{III}L]^{3+}$ complex. In order to get complete thermodynamic information on equation (1), we carried out a voltammetric investigation on a solution of $[Ni^{II}(cyclam)][ClO_4]_2$ and $[Cu^{II}(cyclam)][ClO_4]_2$ complexes in 4.0 mol dm^{-3} $HClO_4$ over the temperature range −12 to +43 °C, using an *isothermal cell* (*i.e.* both working and reference electrodes were kept at the same temperature). The quantity ΔE was found to decrease in a roughly linear way with temperature (see Fig. 2). The slope of the straight line is related to the entropy change ΔS°, associated with equation (1), according to equation (3).

$$d\Delta E/dT = \Delta S^{\circ}/R \qquad (3)$$

Moreover, combination of the free-energy term and entropy term, through the Gibbs–Helmholtz equation (4), gives the

$$\Delta H^{\circ} = \Delta G^{\circ} - T\Delta S^{\circ} \qquad (4)$$

enthalpy contribution associated with redox equilibrium (1). Corresponding thermodynamic quantities in 4.0 mol dm^{-3} $HClO_4$ solution are: $\Delta G^{\circ} = -31$ kJ mol^{-1}, $\Delta H^{\circ} = -46$ kJ mol^{-1} and $T\Delta S^{\circ} = -15$ kJ mol^{-1}. In other words, an especially exothermic enthalpy contribution favours the formation of the trivalent nickel complex, whereas the entropy term favours access to the trivalent state of copper.

It should be noted that the gas-phase process involving the *naked* (unco-ordinated and unsolvated) metal centres [see equation (5)] is strongly displaced toward formation of trivalent

$$Cu^{III}(g) + Ni^{II}(g) \rightleftharpoons Cu^{II}(g) + Ni^{III}(g) \qquad (5)$$

nickel. The ΔE value associated with reaction (5) is related to the difference in the third ionization energies of nickel and copper, $I_3(Cu) - I_3(Ni)$, and is quite large: 154 kJ mol^{-1} (which corresponds to a potential difference of 1.6 V).[11] However, this very large energy difference is reduced nearly to 1/4 when the gaseous metal ions penetrate the cyclam ring and dissolve in water, due to a combination of ligand-field effects and, to a minor extent, of solvation effects This drastic reduction can be accounted for, considering the variation of the electronic configuration of the metal centres and of their stereochemistry, which takes place during reaction (1).

Stereochemical and electronic aspects of the Ni^{III}–Ni^{II} and Cu^{III}–Cu^{II} redox changes in tetraazamacrocyclic complexes have been elucidated in past years through magnetic and spectromagnetic studies[12] and, when possible, by X-ray investigations on isolated crystalline complexes.[2,13,14] In particular, complexes of both Cu^{III} and Ni^{II} (which have a d^8 configuration) are square, low-spin species.* On the other hand, complexes of either Cu^{II} (d^9) or Ni^{III} (d^7, low spin) exhibit an elongated octahedral stereochemistry, the axial sites being occupied by solvent molecules or anions. It has been previously shown, on the basis of crystal-field theory arguments, that co-ordination favours the formation of trivalent copper and disfavours the formation of trivalent nickel. Making the very rough assumption that the *Dq* term is the same for a M^{2+} and a M^{3+} cation, the change from a octahedral copper(II) complex to a planar copper(III) complex involves a favourable crystal field stabilization energy contribution of 16.56 *Dq*, whereas the change from a planar nickel(II) to a octahedral nickel(III) species is disfavoured by 6.56 *Dq* units.[16] Thus, quite strongly co-ordinating ligands, as the quadridentate macrocycle cyclam, which generates especially high values of *Dq*, tend to destabilize Ni^{III} compared to Cu^{III}, as far as bonding terms are concerned.

Stereochemical changes could account for the sign of the entropy change associated with equation (1). In relatively dilute solutions, the redox process under investigation can be described by the metathetic equation (6). Equation (6) shows

$$[Cu^{III}L]^{3+} + [Ni^{II}L]^{2+} + 4H_2O \rightleftharpoons [Cu^{II}L(H_2O)_2]^{2+} + [Ni^{III}L(H_2O)_2]^{3+} \qquad (6)$$

that, moving from left to right, solvent molecules *disappear* from the solution, to be incorporated in the co-ordination sphere of the complexes of Cu^{II} and Ni^{III}. This causes a decrease in the translational entropy, which is reflected by the negative value of ΔS° (−50 J K^{-1} mol^{-1}).

On increasing the acidity, ΔE substantially decreases, indicating that the formation of the trivalent nickel complex, compared to the trivalent copper species, becomes less and less favoured. At $HClO_4 \geqslant 9$ mol dm^{-3} the separation between the two oxidation peaks in the DPV profile is so small that they almost superimpose, preventing the direct determination of ΔE. Therefore, we measured ΔE through an *indirect* method, *i.e.* using the hexamethylcyclam nickel(II) complex $[NiL'][ClO_4]_2$ as an internal standard. The one-electron oxidation of this complex takes places at a potential *ca.* 250 mV more positive than that of $[Ni^{II}(cyclam)]^{2+}$, over the $HClO_4$ concentration range 4.0–11.56 mol dm^{-3}. Thus, at a given $HClO_4$ concentration, a first solution was investigated, which was 10^{-3} mol dm^{-3} both in $[Cu^{II}(cyclam)][ClO_4]_2$ and in $[NiL'][ClO_4]_2$. The separation of the two peaks of the DPV profile was measured: $\Delta E_{Cu} = E_{\frac{1}{2}}([NiL']^{3+/2+}) - E_{\frac{1}{2}}\{[Cu(cyclam)]^{3+/2+}\}$. For instance, in a 9 mol dm^{-3} $HClO_4$ solution, at 25 °C, $\Delta E_{Cu} = 125$ mV. In a second experiment a solution of the same concentration of $HClO_4$ containing equimolar amounts of $[NiL'][ClO_4]_2$ and of $[Ni^{II}(cyclam)][ClO_4]_2$ was employed and the potential difference $\Delta E_{Ni} = E_{\frac{1}{2}}([NiL']^{3+/2+}) - E_{\frac{1}{2}}\{[Ni(cyclam)]^{3+/2+}\}$ was determined. For instance, in a 9 mol dm^{-3} $HClO_4$ solution, at 25 °C, $\Delta E_{Ni} = 253$ mV. Then, the quantity ΔE, associated with the redox equilibrium (1), was calculated from the difference [equation (7)].

$$\Delta E = \Delta E_{Ni} - \Delta E_{Cu} \qquad (7)$$

Fig. 1 reports a plot of ΔE *vs.* the $HClO_4$ concentration: ΔE decreases steeply with increasing $HClO_4$ concentration, to

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* The nickel(II) cyclam complex exists in aqueous solution as an equilibrium mixture of the yellow square-planar, low-spin state, $[Ni^{II}(cyclam)]_2{}^+$, and of the blue *trans*-diaquaoctahedral, high-spin state, $[Ni^{II}(cyclam)(H_2O)_2]^{2+}$.[15] An increase in the temperature and in the concentration of the background electrolyte (*e.g.* $NaClO_4$) favours the formation of the low-spin complex. The blue-to-yellow interconversion can be monitored through the rather intense band of the low-spin species at 454 nm. In 4 mol dm^{-3} $HClO_4$ the band reaches its limiting value (ε 65 dm^3 mol^{-1} cm^{-1}), indicating that 100% of the square-planar complex is present. This is confirmed by the fact that either a further increase in concentration or heating does not increase the intensity of the absorption band at 454 nm.

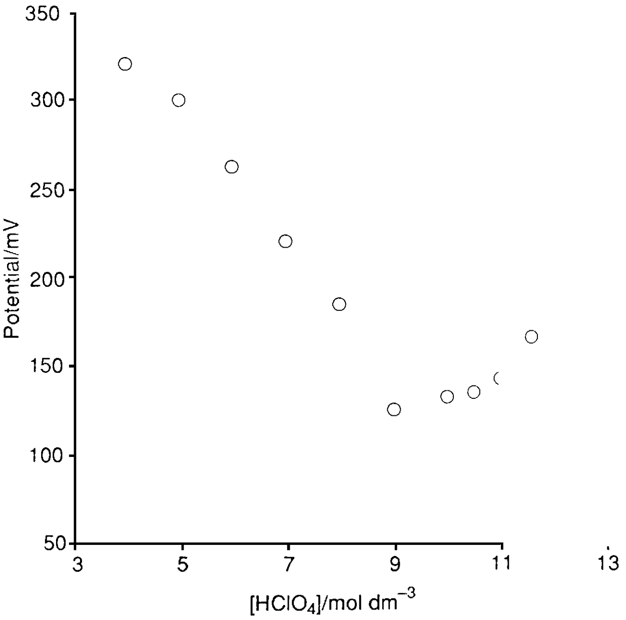

Fig. 1 Variation with the $HClO_4$ concentration of the quantity ΔE, measured at 25 °C: $\Delta E = E_{\frac{1}{2}}\{[Cu(cyclam)]^{3+,2+}\} - E_{\frac{1}{2}}\{[Ni(cyclam)]^{3+,2+}\}$ and is associated with the metathetic reaction $[Cu^{III}L]^{3+} + [Ni^{II}L]^{2+} \rightleftharpoons [Cu^{II}L]^{2+} + [Ni^{III}L]^{3+}$ (L = cyclam)

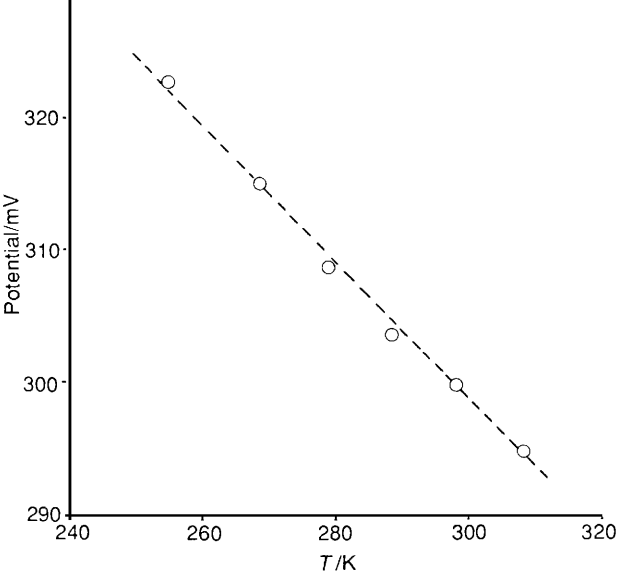

Fig. 2 Temperature dependence of ΔE in a solution 5 mol dm^{-3} in $HClO_4$. The slope is proportional to the entropy change $\Delta S^{\ominus}$ associated with the metathetic reaction given in Fig. 1. At this $HClO_4$ concentration $\Delta S^{\ominus}$ is negative

reach a minimum value around 9 mol dm^{-3}. In other words, the relative stability of the copper(III) state increases and the relative stability of the Ni^{III} decreases with increasing $HClO_4$ concentration. However, at > 9 mol dm^{-3} $HClO_4$, the above trend is reversed, and trivalent nickel begins to stabilize compared to trivalent copper (see Fig. 1).

Change of the relative solution stability of cyclam complexes of Ni^{III} and Cu^{III} with varying electrolyte concentration can hardly be ascribed to electronic effects, but should rather involve modification of the interactions of the medium with the metal–cyclam centres. This consideration prompted us to look at the variation of the entropy change $\Delta S^{\ominus}$ associated with equation (1) with the $HClO_4$ concentration. Therefore, we determined ΔE, for each solution of given $HClO_4$ concentration, at varying temperatures. In a typical experiment, the temperature of an acidic solution 10^{-3} mol dm^{-3} both in $[Ni^{II}(cyclam)][ClO_4]_2$ and $[Cu^{II}(cyclam)][ClO_4]_2$ was varied over the range −15 to +40 °C and the ΔE values were measured at selected temperature intervals.

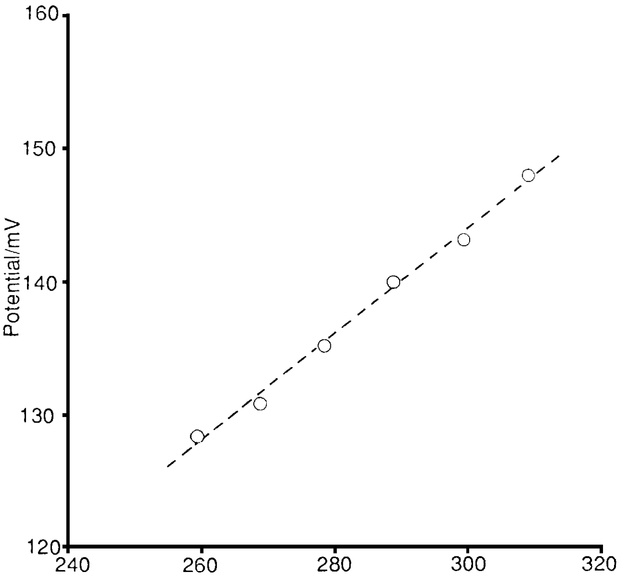

Fig. 3 Temperature dependence of ΔE in a solution 11 mol dm^{-3} in $HClO_4$ (see Fig. 2). At this $HClO_4$ concentration $\Delta S^{\ominus}$ is positive

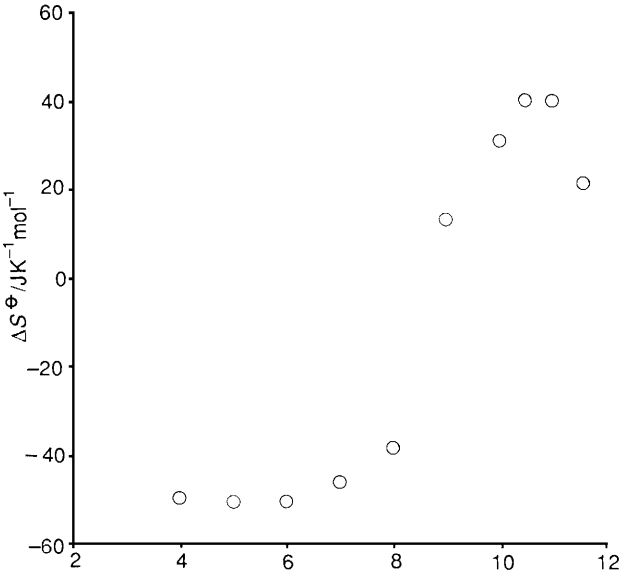

Fig. 4 Variation with the $HClO_4$ concentration of the $\Delta S^{\ominus}$ value, associated with the metathetic reaction in Fig. 1

Fig. 2 shows a plot of ΔE *vs.* T for a solution 5 mol dm^{-3} in $HClO_4$. The least-squares straight line has a negative slope indicating that the $\Delta S^{\ominus}$ value associated with the redox equilibrium (1) is negative. For an $HClO_4$ concentration of $\geqslant 8$ mol dm^{-3}, parallel experiments using $[NiL'][ClO_4]_2$ as an internal standard were performed and, at a given temperature, the ΔE value was calculated as described above. Fig. 3 shows a plot of ΔE *vs.* temperature for a solution 11 mol dm^{-3} in $HClO_4$: notice that in this case that the slope, and the corresponding entropy change, are positive.

Fig. 4 displays the variation with the perchloric acid concentration of the $\Delta S^{\ominus}$ value associated with reaction (1): in less concentrated solution (4–7 mol dm^{-3}) the entropy change is negative and nearly independent of acidity; above an $HClO_4$

concentration of 8 mol dm^{-3}, ΔS° increases steeply, takes a positive value and reaches a maximum at 10–11 mol dm^{-3}. A further increase of the $HClO_4$ concentration to its limiting value (11.56 mol dm^{-3}) makes the ΔS° value decrease. The profile in Fig. 4 can be tentatively explained as follows.

(1) 4–8 mol dm^{-3} $HClO_4$. At this level of concentration the electrolyte anion cannot compete with water, present in overwhelming concentration, for axial sites in the cyclam complexes of Cu^{II} and Ni^{III}. Thus, the redox equilibrium (1) is correctly described through equation (6). The loss of solvent molecules from the solution causes a decrease in translational entropy, which is reflected in the negative value of ΔS° (-50 J K^{-1} mol^{-1}).

(2) 8–11 mol dm^{-3} $HClO_4$. At an electrolyte concentration of 8 mol dm^{-3}, ClO_4^- ions begin to compete seriously for apical co-ordination to Cu^{II} and Ni^{III} (notice that, at this concentration level, there are less than five molecules of water per perchlorate ion). Thus, the investigated reaction should be described, in its limiting situation, as in equation (8). It should be noted that also equation (8) involves the loss of four particles, *i.e.* the four perchlorate ions. Thus, a decrease in translational entropy should occur in the present circumstances, too. However, reaction (8) involves a drastic decrease in the electrical charge, which causes the liberation of water molecules from the hydration spheres of the complexes of Cu^{III} and Ni^{II} and even from that of the ClO_4^- ions. Due to the very poor availability of water molecules in these concentrated solutions (considering also the very special hydrophilicity of the hydrogen ions), this effect cannot be particularly marked, in spite of the dramatic reduction in electrical charge which takes place. However, progressive replacement of water molecules by perchlorate ions in the axial sites of octahedral complexes makes the entropy change ΔS° become first progressively less negative, then zero and finally positive. At an $HClO_4$ concentration of 10–11 mol dm^{-3} a maximum value of $+40$ J K^{-1} mol^{-1} is achieved. However, for the most concentrated solution investigated in this study, 11.56 mol dm^{-3}, the concentration of the $HClO_4$–H_2O azeotropic mixture, ΔS° abruptly decreases. Notice that, at this concentration level, there exist only 2.4 molecules of H_2O per ClO_4^- ion. In other words, we are moving towards a sort of *anhydrous* system, where dehydration effects do not exist anymore and the entropy change ΔS° solely results from the negative translational contribution, associated with the loss of four ClO_4^- ions. Thus, ΔS° exhibits the *regular* negative value, which one could expect in the absence of solvent effects, for instance in the gas phase.

$$[Cu^{III}L]^{3+} + [Ni^{II}L]^{2+} + 4ClO_4^- \rightleftharpoons [Cu^{II}L(ClO_4)_2] + [Ni^{III}L(ClO_4)_2]^+ \quad (8)$$

Conclusion

Previous investigations[6,17,18] had demonstrated that the presence of a strong acid (*e.g.* $HClO_4$) is necessary to stabilize copper(III) complexes of tetraazamacrocycles in aqueous solution: this effect was related to the quenching of a base-promoted step, in the decomposition pattern of the strongly oxidizing complex, *i.e.* was related to the *kinetic* side of the solution stability. This work has shown that perchloric acid, as a background electrolyte, has further effects, of *thermodynamic* nature, on the solution stability of Cu^{III} and of the reference metal centre Ni^{III}. Those effects are related to the ability of the ions of the electrolyte to subtract water molecules from the solution, thus *dehydrating* the electroactive species. In general, such effects are expected to be important for any half-reaction involving metal centres, in which the oxidized and reduced forms differ in the number of co-ordinated solvent molecules.

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