The tetranuclear copper(n) complexes \([\mu_4\text{O}]_4\text{L}_4\text{Cu}_4\text{Cl}_4\] with \(L\) typically being a pyridine derivative, have been reported in the literature since the mid 1960s. Their structures, spectrochemical, thermal, and magnetic behaviours have been subjected to extensive investigation. Structurally, these complexes are adamantane-like, with four Cu centres of distorted trigonal-bipyramidal geometry bridged in pairs by Cl atoms, a central tetrahedral oxygen and one organic ligand co-ordinated to each copper. Davie's and co-workers found that these complexes have Cu atoms that can be successively and stoichiometrically replaced with other metal atoms without altering the overall geometry. This process, known as transmetalation, is accomplished using reagents called transmetallators and can be used to give families of heteropolymetallic (HPM) products as given by equation (1). In this equation NS is S-methyl isopropylidenehydrazinecarbodithioate, \(L\) is a nitrogen-donor ligand such as monodentate \(N,N\)-diformyl-2,4-pyridine (denc) or pyridine (py), and \(M\) is a metal such as Ni, Co or Zn. The transmetalation phenomenon and its requirements, patterns and products have been well established.

Previous electrochemical studies of \([\mu_4\text{O}]_4\text{L}_4\text{Cu}_4\text{Cl}_4\] \(L = \text{denc}\) or \(\text{py}\) had suggested that these complexes are electrochemically inactive. The only reported exception to this finding was for the related complexes \([\mu_4\text{Y}]_4\text{L}_4\text{Cu}_4\text{Cl}_4\] \(L = \text{denc}\) or \(\text{py}\) which exhibited quasi-reversible cyclic voltammetry (CV) at a platinum electrode in dimethyl sulfoxide with 0.20 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. At potentials more negative than \(-1.0\) V the complexes are electrodeposited as Cu-Ni alloy and metal oxide films and display a complicated set of cyclic voltammographs. The voltammographs of all the Cu-containing complexes show a quasi-reversible redox couple in the potential range 0.250 to \(-0.450\) V vs. Ag-AgCl (0.01 M) in CH_2Cl_2. As the number of Cu atoms decreases in the complex, the peak currents \(I_{pa}\) and \(I_{pa}\) decrease proportionally and the peak potential shifts anodically.

The cyclovoltammetric (CV) results indicate that electron transfer initially occurs only to the Cu\({}^\text{II}\) centres and that the electron-transfer reaction appears to be quasi-reversible. Using steady-state voltammetry at an ultramicroelectrode in combination with chronoamperometry at a microelectrode and exhaustive electrolysis shows that one quarter of the Cu atoms remain in the Cu\({}^\text{II}\) form and that the Cu\({}^\text{II}\) complex remains stable. Since only a single CV peak results for all of the complexes, the electron transfer is most likely consecutive with very closely spaced \(E\) potentials. A model based on statistically determined electron transfer to Cu\({}^\text{II}\) in particular faces is also proposed.

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Recent work in our laboratory has shown that, in addition to being electroactive, the series of \([\mu_4\text{O}]\text{denc}_4\text{Cu}_4\text{M}_x\text{Cl}_{12}\] complexes with \(x = 0-4\) when dissolved in dimethyl sulfoxide (dmoso) with 0.20 M tetrabutylammonium hexafluorophosphate as electrolyte can be used as single-source (unimolecular) precursors to deposit electrochemically Cu-Ni alloy and metal oxide films whose net deposition stoichiometry is controlled by the metal stoichiometry of the precursor.

This controlled unimolecular electrodeposition technique may hold the key for producing new types of alloy and mixed-metal oxide films for use in catalysis, microelectronics, magnetic recording media, or other systems in which a well defined atomic-level deposition of metals and metal oxides is required. This process could also lead to new more environmentally benign metal plating technologies.
paper we report on the electrochemical behaviour of the homologous series of the Cu-Ni heteropolymeric complexes obtained from the transmetallation reaction (1). In addition to the synthesis, physical properties and spectra 

for HPM complexes, their thermolytic and electrochemical deposition have also been described.

**Experimental**

All electrochemical work with the exception of the steady-state voltammetry was conducted with E & G Princeton Applied Research Models 273 and 263 potentiostats (E & G, Princeton, N J) both controlled by a DEC P420sx computer and E & G M 270 electrochemical analysis software. All cyclic voltammetry (CV) experiments were run with iR compensation provided by the M 270 software. The steady-state voltammograms were obtained with a Cypress Systems CS-1090 computer controlled electroanalytical system (Cypress Systems, Lawrence, K S).

All experiments were performed with a three-electrode system consisting of a working electrode, platinum counter electrode, and a Ag-AgPF$_6$ (0.01 M)–CH$_3$CN reference electrode, to which all potentials are referenced unless otherwise indicated. Using this reference electrode the peak potential ($E_{pa}$) for 1 M Cu$_2$Cl$_2$(dmap)$-$(0.01 M)–CH$_3$CN was 48 mV. The working electrode for all electrochemical experiments, except the steady-state voltammetry, was a 3 mm diameter (0.071 cm$^2$) platinum disc (BA S, West Lafayette, IN ). The steady-state voltammograms were recorded with a 10 µm diameter platinum disc ultramicroelectrode (Cypress Systems). The working electrodes were polished with 0.05 µm alumina (Buehler), washed with deionized water, sonicated for about 5 min and dried before use. The electrolytic cell was routinely tested and considered acceptable when the anodic and cathodic peak separation was 50 mV.

**Results and Discussion**

**Electroactive species in dmso**

Preliminary studies showed some differences in the electrochemical behaviour of the complexes in solutions of a coordinating solvent such as dmso and a non-coordinating solvent such as methylene chloride. The nature of the electroactive species for the five members of the homologous series of copper-nickel complexes [($\mu$-O)(denc)$\text{Cu}_x\cdot\cdot\cdot\text{Ni(H}_2\text{O)}_x\text{Cl}_y] (x = 0–4) in dmso or methylene chloride was addressed with electron spectroscopy and nuclear magnetic resonance (NMR) measurements.

![Fig. 1](image)

**Fig. 1** The electronic spectra of 0.7 mM [($\mu$-O)(denc)$\text{Cu}_x\cdot\cdot\cdot\text{Cl}_y]$ in dmso (——) and methylene chloride (— — —).

**Results and Discussion**

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trigonal bipyramid to six-co-ordinate pseudo-octahedral is consistent with the observed reduction in spectral intensity associated with the d–d transitions of the CuII centres. Methylene chloride dilutions of dmso solutions of the complexes are consistent with reversible addition of dmso to the coordination sphere of the CuII centres. While it was not possible to identify co-ordinated water in solution it is reasonable to expect that water co-ordinated to the NiII centres can be replaced with dmso. Most importantly, the absence of free amide for (CD$_3$)$_2$SO solutions of the complexes as well as the reversible co-ordination of dmso in CH$_2$Cl$_2$–dmso solutions of the complexes support the conclusion that these complexes remain intact and tetranuclear in dmso and contain one dmso molecule per CuII as the electroactive species according to equation (2).

\[
\begin{align*}
&\left[\left(\mu_4-O\right)\left(denc\right)\left(N\left(H_2O\right)\right)\left(Cu\right)\right]_x(C1)Cl_x + (4 - x)dmso \rightarrow \\
&\left[\left(\mu_4-O\right)\left(denc\right)\left(dmso\right)\left(N\left(H_2O\right)\right)\left(Cu\right)\right]_x(C1)Cl_x \\
&\text{(2)}
\end{align*}
\]

**General electrochemical behaviour in dmso**

Shown in Fig. 2(a)–2(e) are multiple-scan cyclic voltammograms obtained for the five members of this homologous series of Cu–Ni complexes in the potential range 0.25 to –1.80 V and at a scan rate of 0.05 V s$^{-1}$. Each scan was paused at the switching potential for 0, 10, 20, 40 and 100 s. The first scan was taken after cleaning and polishing the electrode while the rest of the scans are continuous. The anodic and cathodic potential limits of 0.25 and –1.80 V, respectively, were necessitated by two processes occurring past these points. If the starting potential is more anodic than about 0.25 V, an initial oxidation current is observed and subsequent peaks during the scan become increasingly irreproducible, most likely due to an oxidation product adsorbed on the electrode surface. The cathodic limit occurs due to the reduction of the supporting electrolyte at potentials greater than –2.4 V and to the bulk electrodeposition of the metals from the complex (deposition of even a very thin Cu–Ni film affects the reproducibility of the electrode and its effects can only be reversed by polishing).

This series of cyclic voltammograms (Fig. 2) dramatically demonstrates the changes caused by the sequential substitution of Cu by Ni in the Cu$_4$ core complex. Two significant changes are observed as the number of Ni atoms in the core increases. First, there is a systematic decrease and disappearance of the redox couple centred at about 0.1 V (C1, A1). As will be shown later, this couple is due to solution electrochemistry and results from the reduction of CuII to stable CuI centres within the complex. Secondly, the anodic peaks between –0.2 and –0.4 V (A7, A8) disappear and a new single narrow peak (A6) appears at –0.6 V, proportional to the increase in the number of Ni centres.

The formation of a deposit on the electrode surface during the CV is readily visible in the voltammogram for each complex. For the Cu$_4$ and Cu$_3$Ni complexes, two anodic peaks [A8, A7; Fig. 2(a) and 2(b)] predominate and both linearly increase with pause time. A parallel situation is also observed for the Ni$_4$ and Cu$_2$Ni$_2$ complexes but with only a single anodic peak [A6; Figs. 2(d) and 2(e)]. As might be expected, the Cu$_2$Ni$_2$ complex shows the most complicated ‘mixed’ behaviour, but the collection of peaks between A8 and A5 [Fig. 2(c)] is intermediate.
contamination by unreacted and unseparated Cu$^{4+}$ remaining from the synthesis (about 5%). Several attempts to switching the potential at the cathodic peak current ($i_{pc}$) for the Cu$^{4+}$ complex recorded after switching at a potential at $-0.6, -1.0, -1.3, -1.6$ and $-2.0$ V. The resulting voltammograms become increasingly more complex, with multiple anodic and cathodic peaks appearing at the more cathodic switching potentials. Switching at $-0.6$ V produces a simple and easily reproducible redox couple whose peak heights decrease in proportion to the number of Cu atoms in the complex. Switching just past the second cathodic peak at $-1.0$ V (C2) does not result in a corresponding anodic peak, indicating both the lack of deposition and reversible electrochemical behaviour. Peak C2 does not increase with scan rate and thus may be the result of an adsorbed species. Switching at a potential $> -1.3$ V, slightly cathodic of C3, results in the appearance of three anodic peaks (A5, A7, A8) which increase proportionally to the amount of time spent cathodic of C3 (see Fig. 2(a)).

Solution electrochemistry

Owing to the complexities involved in studying such complicated electrodeposition processes as these, we limited our preliminary investigations mainly to the initial steps of the reduction processes for the redox couple shown in Fig. 2 (C1, A1). As before, the initial and switching potentials were chosen to eliminate, to the maximum extent possible, any interferences from the adsorption of oxidation products at the anodic end and the formation of Cu-Ni films at the cathodic end. Repetitive cycling between 0.25 and $-0.45$ V showed no difference between the first and fifteenth scan for any of the complexes. This indicates that coverage of the electrode surface with adsorbed oxidation products and/or electrodeposited metals did not occur and the CV redox couple is due entirely to solution electrochemistry.

A typical example of the cyclic voltammograms obtained for each complex in the potential range of 0.25 to $-0.45$ V at a scan rate of 0.05 V s$^{-1}$ is shown in Fig. 4. The dependence of the cathodic peak current ($i_{pa}$) and peak potential ($E_{pa}$) on the Cu-Ni stoichiometry of the complexes is graphically shown in Fig. 5(a) and 5(b), respectively. In general, both $i_{pa}$ and $E_{pa}$ decrease linearly in proportion to the decrease in the number of Cu atoms. However, $i_{pa}$ for a given complex is not as reproducible and is probably more easily perturbed by the adsorption process occurring at the switching potential. The cyclic voltammogram for the Ni$_2$ complex shows a small peak which is due to contamination by unreacted and unseparated Cu$_4$ complex remaining from the synthesis (about 5%). Several attempts to eliminate the Cu$_4$ complex residue were unsuccessful.

The anodic and cathodic peak potentials ($E_{pa}$ and $E_{pc}$) both independently exhibit an apparent non-linear relationship with the number of Ni atoms. Both peaks shift to more anodic potentials and become broader and closer together as the number of Ni atoms increases. This apparent non-linear behaviour is most likely due to the Cu$_4$ complex contamination which represents an increasing fraction of the Cu species in the samples and which we suspect is responsible for both slightly broadening and cathodically shifting the CV peaks. The contamination represents only about 7% of the total Cu$^{4+}$ in the Cu$_4$Ni complex sample and thus has very little effect on the CV peak potential in this case. However, it represents 10% of the CuNi$_3$ contamination and 17% of the CuNi$_2$ contamination. The CV peak seen for the Ni$_2$ complex is due entirely to the Cu$_4$ contamination. If we adjust the shift of the peak potential in

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Fig. 3 The effect of switching potential on the anodic sweep for the CV of a 1 mM solution of [(μ$_4$-O)(denc)$_4$Cu$_4$Cl$_4$] in dmso–NBu$_4$PF$_6$ (0.20 M) with $v = 0.02$ V s$^{-1}$

Several of the other cathodic and anodic peaks also show some very slight changes, most likely due to some residual deposit remaining on the electrode surface after each scan.

Owing to the complexity seen in the voltammograms above, the redox electrochemistry was further investigated by varying the switching potential. Shown in Fig. 3 are the superimposed cyclic voltammograms for the Cu$_4$ complex recorded after switching at the switching potential. The cyclic voltammograms become increasingly more complex, with multiple anodic and cathodic peaks appearing at the more cathodic switching potentials. Switching at $-0.6$ V produces a simple and easily reproducible redox couple whose peak heights decrease in proportion to the number of Cu atoms in the complex. Switching just past the second cathodic peak at $-1.0$ V (C2) does not result in a corresponding anodic peak, indicating both the lack of deposition and reversible electrochemical behaviour. Peak C2 does not increase with scan rate and thus may be the result of an adsorbed species. Switching at a potential $> -1.3$ V, slightly cathodic of C3, results in the appearance of three anodic peaks (A5, A7, A8) which increase proportionally to the amount of time spent cathodic of C3 (see Fig. 2(a)).

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Fig. 4 Cyclic voltammograms at a platinum electrode for 1 mM solutions of the (a) Cu$_4$, (b) Cu$_4$Ni, (c) Cu$_2$Ni$_2$, (d) CuNi$_3$ and (e) Ni$_4$ core complexes in dmso–NBu$_4$PF$_6$ (0.02 M) with $v = 0.05$ V s$^{-1}$

The anodic and cathodic peak potentials ($E_{pa}$ and $E_{pc}$) both independently exhibit an apparent non-linear relationship with the number of Ni atoms. Both peaks shift to more anodic potentials and become broader and closer together as the number of Ni atoms increases. This apparent non-linear behaviour is most likely due to the Cu$_4$ complex contamination which represents an increasing fraction of the Cu species in the samples and which we suspect is responsible for both slightly broadening and cathodically shifting the CV peaks. The contamination represents only about 7% of the total Cu$^{4+}$ in the Cu$_4$Ni complex sample and thus has very little effect on the CV peak potential in this case. However, it represents 10% of the CuNi$_3$ contamination and 17% of the CuNi$_2$ contamination. The CV peak seen for the Ni$_2$ complex is due entirely to the Cu$_4$ contamination. If we adjust the shift of the peak potential in
propportion to the contamination (i.e. 7, 10, 17 and 100% more anodic from the Cu₄ potential), the peak potentials present a more linear relationship with increasing Ni content as shown in Fig. 5(b). From this anodic shift one may infer that it becomes slightly easier to transfer electrons as the Cu Ni is replaced by Ni in the core structure.

The peak separation (ΔE_p) of the redox couple between 0 and -200 mV (Fig. 2, peaks C1, A1 and Fig. 4) for each complex was also studied as a function of the CV sweep rate (v). This redox couple for all Cu–Ni complexes displayed the diagnostic criteria expected of a quasi-reversible charge-transfer system. On the Pt electrode, for v = 0.01-20 V s⁻¹ the ΔE_p separation varied linearly from 120 to 800 mV, with the current function i(vs.) being constant and independent of v, with peak broadening and the ratio i_p/i_{peak} = 1. Recent preliminary studies (to be published in a separate paper) indicate that the CV of this couple, at a hanging mercury drop electrode, is reversible with ΔE_p = 60 mV and a consecutive three-electron transfer.

### Determination of the number of electrons transferred and the diffusion coefficients

The CV results obtained above appear to indicate that electron transfer initially occurs only to the Cu¹⁺ and the ratio i_p/i_{peak} = 1. Recent preliminary studies (to be published in a separate paper) indicate that the CV of this couple, at a hanging mercury drop electrode, is reversible with ΔE_p = 60 mV and a consecutive three-electron transfer.

### Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>Method A</th>
<th>Method B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁴</td>
<td>3.1 ± 0.2</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>CuNi</td>
<td>2.0 ± 0.2</td>
<td>2.4 ± 0.3</td>
</tr>
<tr>
<td>CuNi₂</td>
<td>2.0 ± 0.2</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>CuNi₃</td>
<td>0.62 ± 0.1</td>
<td>1.5 ± 0.3</td>
</tr>
</tbody>
</table>

* Recalculated from Method A data.

### Fig. 6

The chronoamperometric (----) and chronocoulometric (---) response for exhaustive electrolysis of 8 cm³ of 1 mM [µ₄-O]-[(denC)CuCl₂] in dmso–NBu₄PF₆ (0.20 M) at a large mercury-pool working electrode with a Pt counter electrode and a Ag-AgCl electrode. Solution was stirred and kept under N₂ during electrolysis.

### Fig. 7

The electronic spectrum for the d-d transition of Cu⁴⁺ in the complex for the electrolysis shown in Fig. 6 taken at t = 0 (---) and 14.4 ks (-----).

Pt microdisc electrode and equation (4). The value of n of the ferrocene-ferrocenium couple was taken to be 1. The average of three experimentally determined values of n and D are shown in Table 1, Method A.

In a recent study of ligand effects on the ([µ₄-O]L₄CuCl₂) complexes, we determined n and D by exhaustive electrolysis (chronoamperometry) and spectroscopic monitoring of the electrolysis products. The results for the ([µ₄-O]L₄CuCl₂) complex are of particular interest for this study and were thus supplemented by several additional replications which are presented here in brief summary. Fig. 6 shows a typical example of the chronoamperometric and chronocoulometric response obtained during the exhaustive electrolysis. The average values calculated from five replicate samples were n = 3.1 ± 0.1 and D = (2.2 ± 0.1) × 10⁻⁶ cm² s⁻¹. The noise recorded during the electrolysis and over extensive periods (generated most likely by the stirring) was random, appearing at different time intervals for all samples studied with no significant effect on the overall measured charge. The most interesting aspect of this experiment is revealed when we combine the results of the exhaustive electrolysis with those of the accompanying spectroscopic analysis of the products. Fig. 7 shows the electronic spectrum for the d-d transition of Cu⁴⁺ in the complex taken before and after 4 h of exhaustive electrolysis. The average of two measurements gives an absorbance of 0.29 before and 0.080 after electrolysis. This indicates that 27% of the copper atoms are still in the CuCl₂ form. Since the electrolysis appears complete we can reasonably assume that these Cu⁴⁺ atoms reside as single centres in the ([µ₄-O]L₄CuCl₂) complex.

To improve the reliability of n and D further, we then used the average value of D determined from the above exhaustive
The number of electrons determined above for this initial redox couple varies roughly from \( n = 3 \) for the Cu complex to \( n = 0.6 \) for the CuN complex. Since only a single CV peak results for all of the complexes (Fig. 2, peak C1, A1), the electron transfer is either simultaneous or consecutive with closely spaced \( E^0 \) potentials. A simultaneous three-electron transfer process seems unlikely and should produce a much sharper CV peak. On the other hand, our attempts to isolate individual one-electron steps at fast sweep rates up to 150 V s\(^{-1}\) as suggested by Pierce and Geger &29 and by using differential pulse voltammetry did not resolve this question either. The most reasonable assumption is that we have a consecutive transfer of three electrons with the same or closely spaced \( E^0 \). This assumption has also been borne out by a reasonable fit of the experimental CV data with a simulated cyclic voltammogram using three electrons with very closely spaced \( E^0 \) potentials.

**Proposed model for heterogeneous electron transfer**

As shown in Table 1 and Fig. 4, the addition of electrons to the CuN complex gives a CV redox couple (C1, A1) for which \( n \) and \( n \) appear to correlate with the replacement of the Cu by Ni. If we assume that electron transfer takes place through the ligands directly to the Cu4 centres, then we should expect to see \( n = 4 \) decrease stepwise to \( n = 1 \) as we replace each Cu by Ni. However, as Table 1 clearly shows, this is not the case. To explain why all of the Cu4 centres in \([\mu_4-O](denc)Cu_{4}Cl_{4}]^{2-}\) are not reduced, and to account for the non-integer decrease of \( n \) with increasing Ni content, we propose that the electron transfer takes place between the ligands but instead may take place through three of the bridging chlorines on one ‘face’ of the complex. In addition, once the three electrons are transferred (for the Cu4 complex), the energetics may not allow transfer of the fourth electron at that point or at a later approach.

The number of electrons that can be transferred to each \([\mu_4-O](denc)Cu_{4}Cl_{4}]^{2-}\) species is affected by the redox potential of the electrode and the metal composition of the electrodes. The model proposed for the electron-transfer mechanism gives values of \( n \) in very good agreement with the observed data and accounts for both the electrochemical and spectroscopic observations. It also accounts for the fact that for all four Cu complexes, the electron transfer is chemically reversible and that the Cu-containing complex is stable within the time-frame of the experiments described here. As the potential is scanned to more cathodic potentials, the remaining Cu and Cu centres are reduced at around \(-1.0 \) V and eventually the Ni centres are reduced at about \(-2.0 \) V. As reported in previous work, for the deposits made between \(-2.0 \) to \(-2.2 \) V, both XRD and ESCA investigations of the electrode surface have conclusively shown that this deposited hard metallic-like film consists mainly of Cu-Ni alloy, CuO, NiO and Ni(OH)\(_2\), with the proportions varying with the metal content of the complex. From this data and from results of the partial anodic scans (Fig. 3), the three anodic peaks (A6, A7 and A8) in Fig. 2 can be assigned to the reoxidation of the deposited material via Cu-Ni \( \rightarrow \) Cu-Ni, Cu-Ni \( \rightarrow \) Cu-Ni and Cu-Ni, respectively.

The electrochemistry of these heteropolymeric complexes is unique in that the electron transfer appears to be consecutive and at about the same potential (on a Pt electrode) and may even be electrochemically reversible and consecutive on a mercury electrode. Further studies are needed to examine the number of electrons transferred using exhaustive electrolysis for the CuN and CuNi complexes. Total electrolysis of these complexes with a resulting \( n = 3.0 \), 2.0 and 1.0, respectively, would put in doubt the orientation hypothesis while \( n = 2.25 \), 1.50 and 0.75 would certainly lend weight to some sort of orientation or adsorption driven reaction.

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