Electrochemical and Electron Spin Resonance Studies of Dichloro(1,2,4-triazole)copper(II) and Dichlorobis(1,2,4-triazole)copper(II) in Dimethyl Sulphoxide†

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An electrochemical and e.s.r. characterization of [Cu(Hta)Cl$_2$] and [Cu(Hta)$_2$Cl$_2$] (Hta = 1,2,4-triazole) was carried out in dimethyl sulphoxide. Molar conductance data indicate that one Cl$^-$ ion is dissociated from each species which exist as 1 : 1 electrolytes in Me$_2$SO. Both complexes undergo two one-electron reductions in Me$_2$SO. The first is reversible and occurs at 0.33 and 0.34 V *vs.* saturated calomel electrode (s.c.e.) respectively. The second reduction is irreversible and occurs in either one or two steps both of which result in deposition of copper metal onto the platinum electrode surface. These reactions occur at E_p values between −0.54 and −0.66 V depending upon the scan rate. *In situ* e.s.r. spectra recorded during bulk controlled-potential reduction of [Cu(Hta)Cl$_2$] indicate that the singly reduced species undergoes a dissociation of one Hta ligand which then binds to unreduced [Cu(Hta)Cl$_2$] to form higher-co-ordination-number complexes of the type [Cu(Hta)$_n$Cl]$^+$ where n = 3 or 4. The frozen-solution e.s.r. spectrum of [Cu(Hta)Cl$_2$] in Me$_2$SO has an anisotropic signal at $g_{\parallel}$ = 2.377 with $A_{\parallel}^{Cu}$ = 128 G and $g_{\perp}$ = 2.090. No superhyperfine structure in $g_{\perp}$ is observed. These e.s.r. parameters are similar to those of CuCl$_2$ in Me$_2$SO suggesting that the Hta ligands of [Cu(Hta)Cl$_2$] are only weakly bonded to the Cu^{II} in solution. The spectrum of [Cu(Hta)$_2$Cl$_2$] exhibits a decreased value of $g_{\parallel}$ (2.297) and an increased value of $A_{\parallel}^{Cu}$ (166 G) with respect to [Cu(Hta)Cl$_2$], consistent with the presence of a stronger equatorial ligand field in the former complex. An overall electroreduction mechanism for [Cu(Hta)Cl$_2$] and [Cu(Hta)$_2$Cl$_2$] is proposed on the basis of the voltammetric and e.s.r. data and comparisons are made with data for CuCl$_2$ under similar solution conditions.

Both dichloro(1,2,4-triazole)copper(II), [Cu(Hta)Cl$_2$], and dichlorobis(1,2,4-triazole)copper(II), [Cu(Hta)$_2$Cl$_2$] (Hta = 1,2,4-triazole) have been investigated in the solid state.[1–5] An X-ray crystal structure of [Cu(Hta)Cl$_2$] shows that the neighbouring nitrogen atoms of one triazole molecule co-ordinate to two copper atoms which are bridged by two chlorine atoms to form an infinite linear chain in the crystals.[6] A simplified chain structure of this compound is shown in Figure 1. The magnetic moment of the complex in the solid state indicates a complete absence of spin interaction between the copper atoms at room temperature.[7] However, at low temperature, the complex is antiferromagnetic and a superexchange interaction exists between the neighbouring spins in a given chain.[8] E.s.r., i.r., and u.v.–visible spectra of [Cu(Hta)Cl$_2$] and [Cu(Hta)$_2$Cl$_2$] have also been reported in the solid state,[2,4,9a] but the results of i.r. and u.v.–visible studies are incomplete.[2] The exact structure of [Cu(Hta)$_2$Cl$_2$] is not clear but it is probably polynuclear.[2,9b]

Virtually all studies of [Cu(Hta)Cl$_2$] or [Cu(Hta)$_2$Cl$_2$] have focused on their properties in the solid state. Some electrochemistry of Fe, Co, Ni, Cu, Zn, and Cd complexed with 1,2,4-triazole in aqueous media has been reported,[10] but few details on the copper(II) complexes were provided. There have been no other reports on the chemical behaviour or physicochemical characterization of these species in solution. Thus, this present paper presents both the first electrochemistry and the first e.s.r. spectroscopy of [Cu(Hta)Cl$_2$] and [Cu(Hta)$_2$Cl$_2$] in non-aqueous media.

Experimental

Chemicals.—Dichloro(1,2,4-triazole)copper(II) and dichlorobis(1,2,4-triazole)copper(II) were synthesized according to methods described in the literature.[2] Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Inc. Woodside, New York (Found: C, 12.10; H, 1.45; Cl, 34.80; Cu, 31.00; N, 20.75. Calc. for C$_2$H$_3$Cl$_2$CuN$_3$: C, 11.8; H, 1.50; Cl, 34.85; Cu, 31.20; N, 20.65. (Found: C, 17.70; H, 2.25; Cl, 26.05; Cu, 23.05; N, 30.75. Calc. for C$_4$H$_6$Cl$_2$CuN$_6$: C, 17.65; H, 2.20; Cl, 26.00; Cu, 23.30; N, 30.85%).

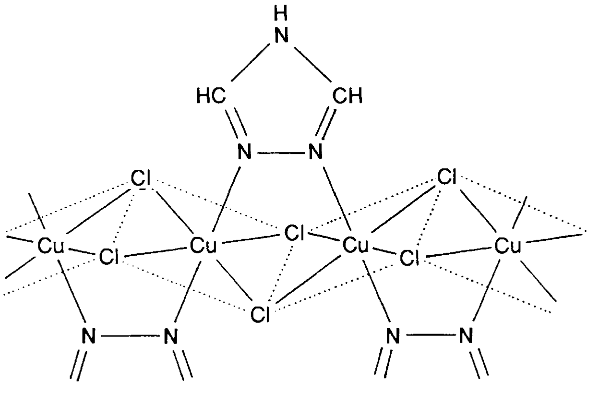

Figure 1. Simplified chain structure of [Cu(Hta)Cl$_2$] in the solid state

1,2,4-Triazole and tetra-n-butylammonium chloride were purchased from Fluka and Aldrich Chemical Co., respectively,

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† *Non-S.I. unit employed:* G = 10^{-4} T.

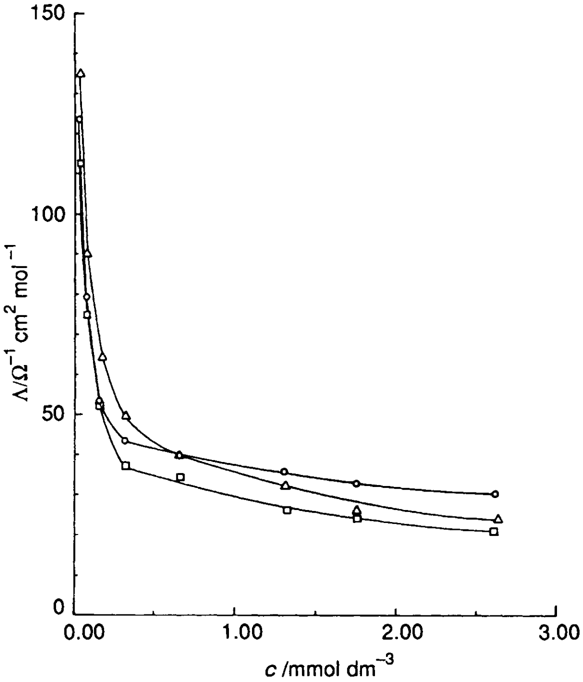


Figure 2. Molar conductance of $NBu^n{}_4ClO_4$ (○), $[Cu(Hta)_2Cl_2]$ (△), and $[Cu(Hta)Cl_2]$ (□) at different concentrations in Me_2SO

and used without further purification. Spectrophotometric grade quality dimethyl sulphoxide was vacuum-distilled over 4-Å molecular sieves before use. Unless otherwise stated, the solvents contained 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate as supporting electrolyte. This salt was purchased from Fluka Chemical Co., twice recrystallized from ethyl alcohol, and stored in a vacuum oven at 40 °C. Anhydrous copper(II) chloride and copper(I) chloride were purchased from Alfa Products and Fisher Scientific Co., respectively.

Instrumentation.—Cyclic voltammetric measurements were made with an IBM 225 voltammetric analyzer and a conventional three-electrode system. The working electrode was a platinum button 0.88 mm^2 in area. A saturated calomel electrode (s.c.e.) was used as the reference electrode for all electrochemical experiments. Rotating-disk voltammetry was performed with a Pine Instrument MSR speed controller coupled to a Pine Instrument RDE4 potentiostat.

A Princeton Applied Research model 173 potentiostat/179 coulometer system was used for bulk controlled-potential coulometry. Current–time curves were recorded with a PAR model RE0074 X-Y recorder. Two large coiled platinum-gauze electrodes were used for the anode and cathode and were separated by means of a fritted glass disk.

In situ e.s.r. measurements were performed with a column-shaped thin-layer e.s.r. spectroelectrochemical cell whose design and application has been described.[11,12] The electrolysis was carried out at room temperature but the e.s.r. spectra were recorded at low temperature. Room-temperature e.s.r. spectra were taken in a flat cell purchased from Wilmad Glass Co. E.s.r. spectra were recorded on an IBM model ER-100D system. The magnetic field position was determined with diphenylpicrylhydrazyl (dpph) (g = 2.0036). Conductivity measurements were performed with the aid of a YSI model 31 conductivity bridge.

Results and Discussion

Conductivity and Electrochemistry.—The complexes $[Cu(Hta)Cl_2]$ and $[Cu(Hta)_2Cl_2]$ have polynuclear structures in the solid state.[2,6] However, both complexes exist as monomers in Me_2SO and show a 1:1 dissociation as demonstrated by the conductivity data in Figure 2. The compounds $[Cu(Hta)Cl_2]$, $[Cu(Hta)_2Cl_2]$, and $NBu^n{}_4ClO_4$ all have approximately the same molar conductance in the concentration range 1.1×10^{-6}—2.6×10^{-3} mol dm^{-3}. It can therefore be concluded that one Cl^- ion dissociates from $[Cu(Hta)Cl_2]$ and $[Cu(Hta)_2Cl_2]$ under these experimental conditions.

A dissociation of Cl^- from $[Cu(Hta)Cl_2]$ or $[Cu(Hta)_2Cl_2]$ in Me_2SO is not unusual. Copper(II) complexes of the type $[Cu(bbdh)X_2]\cdot H_2O$ [bbdh = 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane, X = Cl^- or Br^-] have been shown to undergo halide dissociation in non-aqueous media such as dimethylformamide (dmf) or MeOH[13] and a similar reaction also occurs for $CuCl_2$ in Me_2SO.[14] This anion dissociation is due to the fact that solvent molecules will strongly co-ordinate to copper(II) complexes of the type investigated in this study.[15] However, for the purpose of discussion, this co-ordination is omitted from the equations where stoicheiometric formulae such as $[Cu(Hta)Cl_2]$, $[Cu(Hta)Cl]^+$, $[Cu(Hta)_2Cl_2]$, or $[Cu(Hta)_2Cl]^+$ are utilized.

Cyclic voltammograms for the reduction of $[Cu(Hta)Cl_2]$ at two different scan rates are shown in Figure 3(*a*). The first reduction [labelled (1)] occurs at $E_{\frac{1}{2}}$ = 0.33 V and gives a separation between the cathodic and anodic peaks which ranges between 110 and 160 mV at scan rates from 0.02 to 0.4 V s^{-1}. Other data for this reduction by cyclic voltammetry are listed in Table 1.

The peak-current ratio for the first reduction, i_{p_a}/i_{p_c}, decreases from a diffusion-controlled value of 1.0 at a scan rate of 0.02 V s^{-1} to 0.69 at a scan rate of 0.40 V s^{-1} and is consistent with a reversible chemical reaction following the first one-electron addition.[16] A change in solution colour from yellow to clear is also observed during the first one-electron reduction but the absorption coefficients are too small to monitor accurately the changes in u.v.–visible spectra during the reduction and reoxidation processes.

Bulk controlled-potential coulometry gives 0.86 ± 0.04 electrons transferred in the initial reduction of $[Cu(Hta)Cl_2]$ at 0.00 V but 1.00 ± 0.02 electrons are abstracted when the same solution is reoxidized at a controlled potential of +0.60 V. A constant coulometric value between 0.9 and 1.0 is then obtained if the solution is repeatedly reduced and reoxidized. The numbers of electrons transferred in the first reduction of $[Cu(Hta)Cl_2]$, and upon repeated reoxidation and rereduction of the same solution are listed in Table 2.

Rotating-disk voltammograms for the reduction of $[Cu(Hta)Cl_2]$ are shown in Figure 4 and suggest that a mixture of complexes with different copper oxidation states is formed when $[Cu(Hta)Cl_2]$ is dissolved in Me_2SO. Specifically, the voltammetric results indicate that about 10% of $[Cu(Hta)Cl_2]$ is in the reduced copper(I) form while about 90% of the complex is in the higher copper(II) oxidation state. This agrees with the data by controlled-potential coulometry discussed above.

The second reduction of $[Cu(Hta)Cl_2]$ occurs at E_p values between −0.54 and −0.57 V for potential scan rates between 0.10 and 0.40 V s^{-1}. At a scan rate of 0.02 V s^{-1} or less this reduction is split into two peaks labelled (2) and (3) in Figure 3(*a*). Bulk controlled-potential electrolysis of $[Cu(Hta)Cl_2]$ at −0.56 V [a potential between peaks (2) and (3)] after an initial reduction at 0.00 V shows the transfer of 1.1 ± 0.1 electrons as metallic copper is deposited onto the electrode surface. No additional current is then obtained when the applied potential is stepped from −0.56 to −0.80 V [a potential negative of peak (3)] after completion of the electrolysis. This is consistent with the complete two-electron reduction of $[Cu(Hta)Cl_2]$ at −0.56

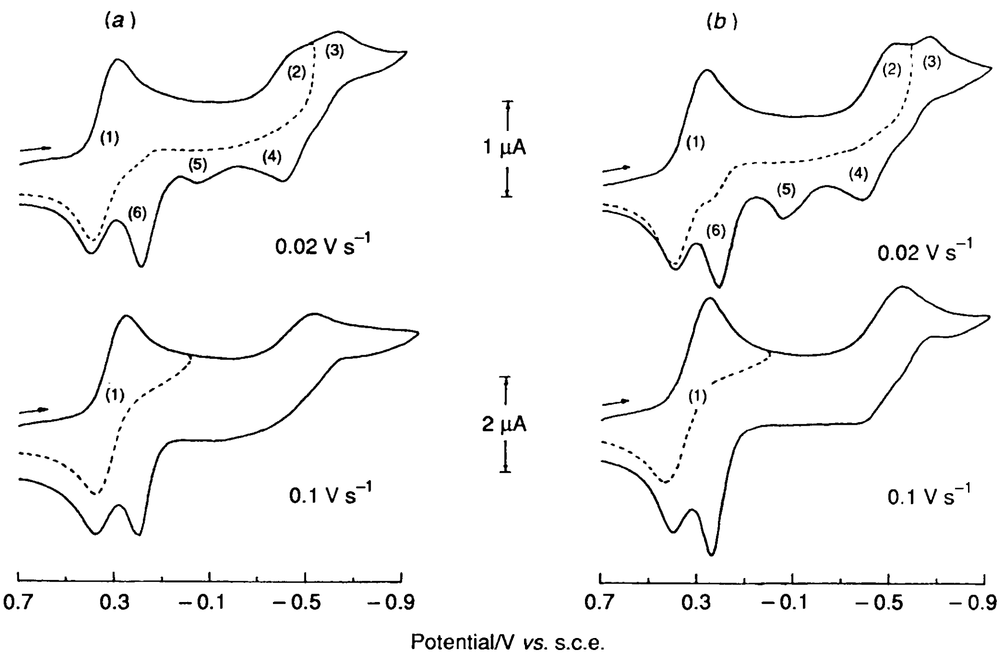


Figure 3. Cyclic voltammograms of 2.5×10^{-3} mol dm^{-3} (*a*) $[Cu(Hta)Cl_2]$ and (*b*) $[Cu(Hta)_2Cl_2]$ in Me_2SO, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ at different scan rates

Table 1. Electrochemical data for the reduction of 2.5×10^{-3} mol dm^{-3} $[Cu(Hta)Cl_2]$ and $[Cu(Hta)_2Cl_2]$ in Me_2SO containing 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$[a]

		First reduction					Second reduction
Compound	Scan rate (V s^{-1})	E_{p_c}	E_{p_a}	ΔE_p[b]	$E_{\frac{1}{2}}$	i_{p_a}/i_{p_c}	E_{p_c}
$[Cu(Hta)Cl_2]$	0.02	0.27	0.38	0.11	0.33	1.00	−0.45[c], −0.65
	0.20	0,26	0.40	0.14		0.75	−0.56
	0.40	0.25	0.41	0.16		0.69	−0.57
$[Cu(Hta)_2Cl_2]$	0.02	0.27	0.41	0.14	0.34	0.94	−0.44[c], −0.66
	0.20	0.23	0.44	0.21		0.73	−0.57
	0.40	0.22	0.46	0.24		0.68	−0.60

[a] All potentials are reported as V *versus* s.c.e. [b] $\Delta E_p = |E_{p_c} - E_{p_a}|$ in volts. [c] $E_{\frac{1}{2}}$ value.

Table 2. Number of electrons calculated by controlled-potential coulometry in Me_2SO containing 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$

	First reduction[a]			Second reduction[b]
Compound	n_{red}	n_{reox}	n_{rered}	n
$[Cu(Hta)Cl_2]$	0.86 ± 0.04	1.00 ± 0.02	0.91 ± 0.06	1.1 ± 0.1
$[Cu(Hta)_2Cl_2]$	0.65 ± 0.06	0.94 ± 0.06	0.91 ± 0.06	1.0 ± 0.1

[a] Process (1) in Figure 3. [b] Process (2) in Figure 3.

V and suggests that two different complexes of copper(I) exist in equilibrium, both of which can be reduced to Cu^0 at a controlled potential of −0.56 V.

The second reduction of $[Cu(Hta)Cl_2]$ is reversible in that the deposited copper metal can be redissolved in Me_2SO upon applying a controlled potential of −0.20 V [a value positive of peak (4)]. Only a small current is then observed independent of whether the potential is stepped from −0.20 to 0.08 V [positive of peak (5)] or from 0.08 to 0.28 V [positive of peak (6)]. However, the original $[Cu(Hta)Cl_2]$ could be recovered by controlled-potential oxidation at 0.60 V.

Similar cyclic voltammetric behaviour is observed for $[Cu(Hta)_2Cl_2]$ and $[Cu(Hta)Cl_2]$ as shown in Figure 3. However, more of the reduced copper(I) form is initially present in Me_2SO solutions of $[Cu(Hta)_2Cl_2]$. Coulometric data indicate that about 1/3 of $[Cu(Hta)_2Cl_2]$ is in the copper(I) form while 2/3 is in the copper(II) form (see Table 2).

Three reductions of $[Cu(Hta)_2Cl_2]$ are observed at a scan rate of 0.02 V s^{-1} while two occur at a scan rate of 0.1 V s^{-1}. The first reduction [(1)] is quasireversible and involves a global one-electron transfer as ascertained by controlled-potential coulometry. A second electron is added during controlled-potential electrolysis at −0.58 V [between peaks (2) and (3)] and, under these experimental conditions, free copper metal is deposited onto the electrode surface.

The potentials for reduction of $[Cu(Hta)Cl_2]$ and $[Cu(Hta)_2Cl_2]$ do not change upon the addition of 1—8 equivalents of free Hta ligand to the solution nor do they change upon the addition

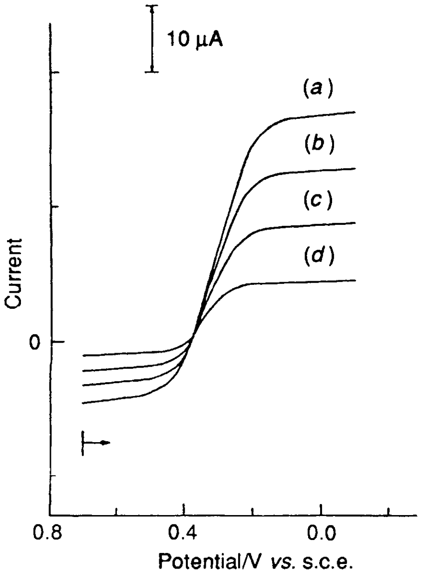


Figure 4. Rotating-disk voltammograms for the reduction of 8.4×10^{-4} mol dm^{-3} [Cu(Hta)Cl$_2$] in Me$_2$SO, 0.1 mol dm^{-3} NBu$^n_4$ClO$_4$: (*a*) 1 600, (*b*) 900, (*c*) 400, and (*d*) 100 revolutions min^{-1}

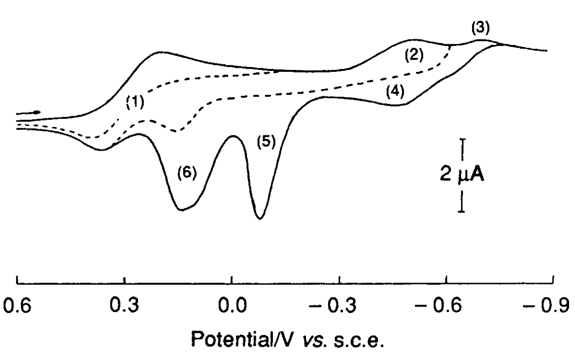


Figure 5. Cyclic voltammogram of 5.2×10^{-3} mol dm^{-3} CuCl$_2$ in Me$_2$SO, 0.1 mol dm^{-3} NBu$^n_4$ClO$_4$. Scan rate = 0.02 V s^{-1}

of 1—7 equivalents of free Cl$^-$ (in the form of NBu$^n_4$Cl). This suggests that there is neither a loss nor gain of co-ordinated ligands upon reduction, and that the electrode reaction on the cyclic voltammetric time-scale occurs as shown in equation (1).

$$[\mathrm{Cu(Hta)}_n\mathrm{Cl}]^+ + \mathrm{e} \rightleftharpoons [\mathrm{Cu(Hta)}_n\mathrm{Cl}]\ [\text{peak (1)}] \quad (1)$$

However, as seen in Table 1, the change of i_{p_a}/i_{p_c} with scan rate is consistent with a reversible chemical reaction following the first electroreduction. As will be shown in the following sections, this chemical reaction involves a conversion of the electrogenerated [Cu(Hta)$_n$Cl] into [CuCl$_2$]$^-$ in solutions of Me$_2$SO.

An assignment of the other voltammetric peaks in Figure 3 comes from cyclic voltammograms of the type shown in Figure 5 for the reduction of CuCl$_2$. This voltammogram closely resembles that of [Cu(Hta)Cl$_2$] and [Cu(Hta)$_2$Cl$_2$] in Me$_2$SO (see Figure 3). The reduction peaks (2) and (3) have similar shapes for all three complexes and are assigned as the reduction of Cu^{I} as shown by equations (2) and (3). Neither peaks (2) nor (3) shift in potential with additon of 1—7 equivalents Cl$^-$ to the solution and this suggests the formation of intermediate [Cu(Hta)$_n$Cl]$^-$ [peak (2)] and [CuCl$_2$]$^{2-}$ [peak (3)] species on the cyclic voltammetric time-scale.

$$[\mathrm{Cu(Hta)}_n\mathrm{Cl}] + \mathrm{e} \longrightarrow \mathrm{Cu} + \mathrm{Cl}^- + n\mathrm{Hta}\ [\text{peak (2)}] \quad (2)$$

$$[\mathrm{CuCl}_2]^- + \mathrm{e} \longrightarrow \mathrm{Cu} + 2\mathrm{Cl}^-\ [\text{peak (3)}] \quad (3)$$

The oxidation peaks (4) and (5) occur at similar potentials for CuCl$_2$, [Cu(Hta)Cl$_2$], and [Cu(Hta)$_2$Cl$_2$]. These reactions are similar to those reported in the literature for the reduction of CuCl$_2$ in Me$_2$SO[14,17] and, for both [Cu(Hta)Cl$_2$] and [Cu(Hta)$_2$Cl$_2$], are assigned as an oxidation of copper metal to Cu^{I} as shown by equations (4) and (5).

$$\mathrm{Cu} + \mathrm{Cl}^- \longrightarrow \mathrm{CuCl} + \mathrm{e}\ [\text{peak (4)}] \quad (4)$$

$$\mathrm{Cu} \longrightarrow \mathrm{Cu}^+ + \mathrm{e}\ [\text{peak (5)}] \quad (5)$$

An oxidation peak (6) also appears in Figures 3 and 5. This peak is not observed after an initial one-electron reduction of the copper(II) complexes by cyclic voltammetry and is only present after deposition of metallic copper onto the platinum electrode. It is also not present in solutions of [Cu(Hta)$_n$Cl]$^+$ containing excess of Cl$^-$ and is assigned as the oxidation of CuCl to [CuCl]$^+$ as shown in equation (6).

$$\mathrm{CuCl} \rightleftharpoons [\mathrm{CuCl}]^+ + \mathrm{e}\ [\text{peak (6)}] \quad (6)$$

E.S.R. Spectra.—Both [Cu(Hta)Cl$_2$] and [Cu(Hta)$_2$Cl$_2$] show a single broad symmetrical e.s.r. signal in the solid state at room temperature. This signal is centred at $g = 2.112$ and 2.102 respectively and agrees with data reported for these compounds in the solid state.[9] However, the two complexes have different solution e.s.r. spectra in Me$_2$SO at both 130 and 299 K.

The frozen-solution e.s.r. spectrum of [Cu(Hta)Cl$_2$] before bulk controlled-potential reduction is depicted in Figure 6(*a*). The copper hyperfine structure of the parallel signal is not resolved but values of $g_{\parallel} = 2.377$ and $A_{\parallel}^{\mathrm{Cu}} = 128$ G can be determined. A superhyperfine structure is not resolvable close to the $g_{\perp} = 2.090$ for concentrations of [Cu(Hta)Cl$_2$] between 3.0×10^{-3} and 1.2×10^{-4} mol dm^{-3}. In addition, the amplitude of the $g_{\perp}$ signal becomes less pronounced at lower concentrations.

The e.s.r. spectra obtained during controlled-potential electrolysis of [Cu(Hta)Cl$_2$] at 0.00 V are shown in Figure 6(*b*)—(*d*). The solution becomes e.s.r. silent when the reduction is complete, consistent with the formation of a copper(I) species in solution. However, stronger $g_{\perp}$ signals are observed as the reduction progresses, and either a seven- or a nine-line superhyperfine structure in $g_{\perp}$ is obtained depending upon how much of the complex has been reduced. In addition, more clearly resolved e.s.r. signals with increased intensity are obtained during the bulk controlled-potential reduction of [Cu(Hta)Cl$_2$]. This may be due, in part, to the formation of a magnetically diluted solution which results from the existence of copper(I) species. The e.s.r. signal reaches a maximum when approximately 86% of the Cu^{II} in [Cu(Hta)Cl$_2$] has been reduced to Cu^{I}. This can be seen in Figure 6(*d*) where the four-line splitting in $g_{\parallel}$ is more clearly resolved and both $g_{\parallel}$ and $A_{\parallel}^{\mathrm{Cu}}$ are significantly changed from the initial spectrum. These spectral data suggest that at least two new e.s.r.-active copper(II) species are formed during bulk electroreduction of [Cu(Hta)Cl$_2$].

An axially symmetric spectrum with $g_{\parallel} > g_{\perp} > g_e$ (2.0023, free-ion value) will result when the unpaired electron of a copper(II) complex resides in the $d_{x^2-y^2}$ orbital.[18] The seven- and nine-line splitting patterns in the $g_{\perp}$ signal of Figure 6(*c*) and (*d*) are consistent with the coupling of Cu^{II} to three and four nitrogens ($I = 1$), respectively. The 15-G coupling constants in Figure 6(*b*)—(*d*) also agree with nitrogen couplings in other copper complexes.[19–21]

Surprisingly, the spectra in Figure 6(*b*) and (*c*) for partially

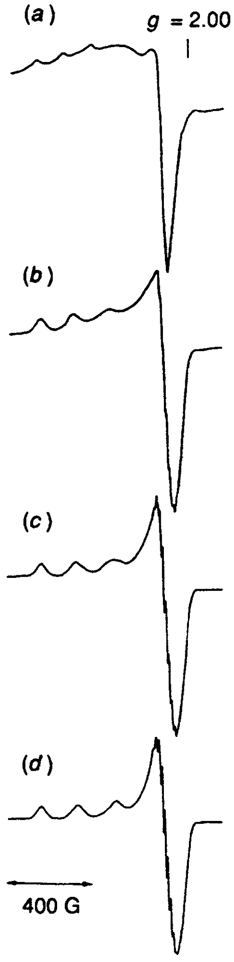


Figure 6. Frozen-solution e.s.r. spectral changes during bulk controlled-potential reduction of 3.3×10^{-3} mol dm^{-3} [Cu(Hta)Cl_2] at 0.0 V in Me_2SO, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$. The percentage of electrolysis and the gain of the e.s.r. spectra (in parentheses) are: (*a*) 0 (3.2×10^5), (*b*) 60 (2.0×10^5), (*c*) 76 (1.6×10^5), and (*d*) 86% (1.25×10^5). In each case, the modulation frequency was 100 kHz and the modulation amplitude was 3.2 G

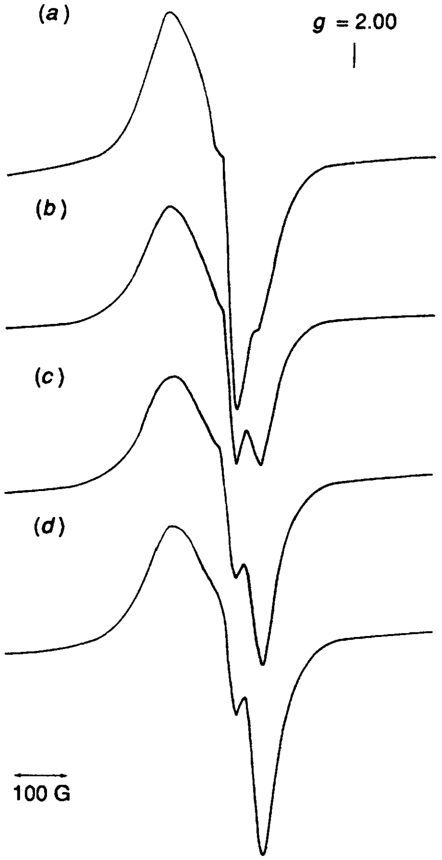


Figure 7. Room-temperature e.s.r. spectral changes of 1.7×10^{-3} mol dm^{-3} [Cu(Hta)Cl_2] in Me_2SO containing the following equivalents of Hta: (*a*) 0.0, (*b*) 1.0, (*c*) 3.0, and (*d*) 5.0

reduced [Cu(Hta)Cl_2] exhibit features which are similar to those for unreduced [Cu(Hta)$_2Cl_2$] in Me_2SO at 130 K (see Figure 8). There is a similarity of the superhyperfine splitting pattern and this suggests that at least one of the new species generated during controlled-potential reduction of [Cu(Hta)Cl_2] has the same structure as the initial [Cu(Hta)$_2Cl_2$] complex in Me_2SO.

The results in Figure 6 are consistent with the stepwise binding of three additional Hta ligands to Cu^{II} during controlled-potential reduction. The excess of Hta ligand could be provided by an exchange reaction involving the initial [Cu(Hta)Cl]$^+$ complex and its product of electroreduction as shown by equations (7)—(9). The Cu^ICl generated in the above

$$[Cu^{II}(Hta)Cl]^+ + [Cu^I(Hta)Cl] \rightleftharpoons Cu^ICl + [Cu^{II}(Hta)_2Cl]^+ \quad (7)$$

$$[Cu^{II}(Hta)_2Cl]^+ + [Cu^I(Hta)Cl] \rightleftharpoons Cu^ICl + [Cu^{II}(Hta)_3Cl]^+ \quad (8)$$

$$[Cu^{II}(Hta)_3Cl]^+ + [Cu^I(Hta)Cl] \rightleftharpoons Cu^ICl + [Cu^{II}(Hta)_4Cl]^+ \quad (9)$$

reaction should be rapidly converted into [CuCl_2]$^-$. This is the most stable form of Cu^I in Me_2SO solutions containing Cl^- [14] and would be a strong driving force for completion of the above three reactions. In this regard, it should be noted that the nine-line e.s.r. spectrum assigned to [Cu(Hta)$_4$Cl]$^+$ in Figure 6(*d*) is only obtained after the controlled-potential reduction of [Cu(Hta)Cl]$^+$ is about 86% complete. This agrees with calculations which indicate that a 75% reduction of the initial [Cu(Hta)Cl]$^+$ complex is required for complete formation of [Cu(Hta)$_4$Cl]$^+$ as shown by equations (7)—(9).

According to the above proposal, the addition of excess of Hta ligand to [Cu(Hta)Cl_2] solutions should also give spectra associated with formation of [Cu(Hta)$_n$$Cl_2$] where n = 2, 3, or 4. This is indeed the case as shown by the data in Figure 7. There is a shoulder in the spectrum at a higher magnetic field before the addition of free Hta ligand to [Cu(Hta)Cl_2]. As the Hta ligand concentration is increased this shoulder increases in intensity and becomes a peak which is attributed to a higher co-ordination number Hta complex in solution. The $g_\perp$ signal in the frozen-solution e.s.r. spectra should show a seven- or a nine-line superhyperfine splitting depending upon how many of the Hta ligands have been complexed by Cu^{II}. In solutions containing between 3 and 6 equivalents Hta only a nine-line superhyperfine splitting in the $g_\perp$ signal is obtained. This indicates that at most four Hta molecules are co-ordinated to the copper atom.

The final copper(II) complex formed during bulk electrolysis of [Cu(Hta)Cl]$^+$ has nine equally spaced lines in the e.s.r. spectrum and one may conclude that four equivalent nitrogens are bound to the Cu^{II}. The decrease of $g_\parallel$ and the increase of $A_\parallel{}^{Cu}$ upon addition of Hta ligand to unreduced [Cu(Hta)Cl_2] solution also suggests that a stronger equatorial ligand field is

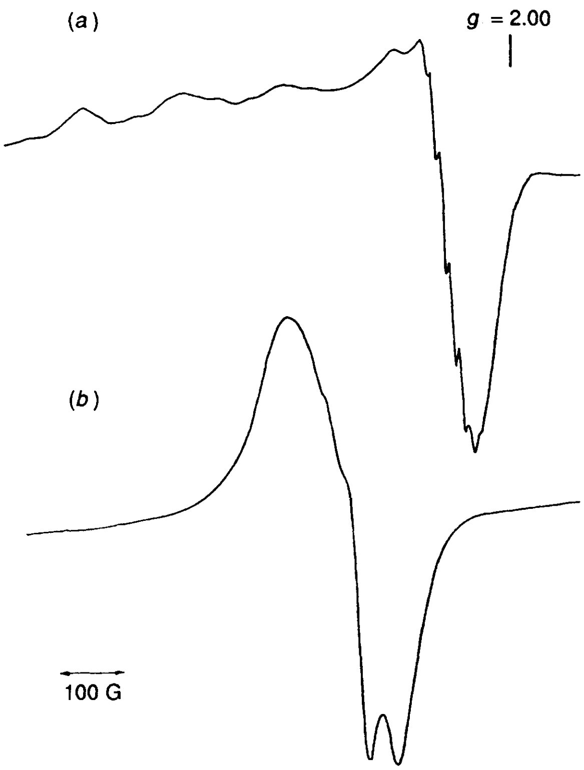
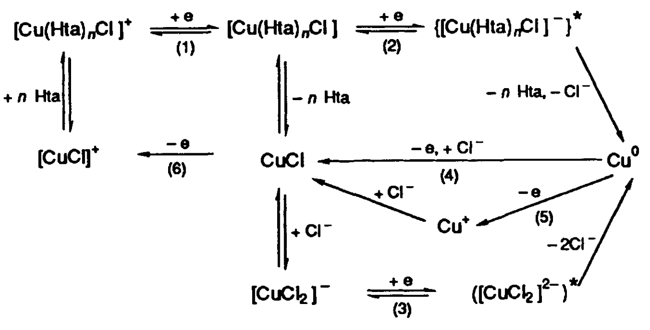


Figure 8. E.s.r. spectra of 8.6 × 10^{-4} mol dm^{-3} $[Cu(Hta)_2Cl_2]$ in Me_2SO at 130 (*a*) and 299 K (*b*)

Table 3. E.s.r. parameters of copper(II) complexes in Me_2SO containing 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ [a]

299 K	130 K



Scheme.

that the Hta molecule is only weakly bound to the Cu^{II} in $[Cu(Hta)Cl_2]$.

The e.s.r. spectral parameters of $CuCl_2$ change only slightly upon addition of 1 equivalent Hta to the solution but the overall spectra under these solution conditions are less clearly resolved. On the other hand, the addition of 2 equivalents Hta results in an e.s.r. spectrum similar to the one obtained for $[Cu(Hta)_2Cl_2]$.

Overall Mechanism for $[Cu(Hta)Cl_2]$ *and* $[Cu(Hta)_2Cl_2]$ *Reduction*.—The electrochemical and e.s.r. results are self consistent and suggest the overall reduction and reoxidation pathway illustrated in the Scheme where the initial complex is represented as $[Cu(Hta)_nCl_2]$ ($n = 1$ or 2). The proposed intermediates are based on the lack of dependence of peak potentials on Cl^- or Hta and are shown by an asterisk.

Both $[Cu(Hta)Cl_2]$ and $[Cu(Hta)_2Cl_2]$ exist as dissociated 1:1 complexes in Me_2SO and both are reduced *via* an overall two electrons to give copper metal and free Hta ligand as final products. At low scan rates, the overall redox reactions proceed as shown in equations (1)—(6). In contrast, the reactions are less complicated at faster potential scan rates or in the presence of excess of Cl^- or Hta ligand. Under these conditions, peaks (3), (5), and (6) are not present and the oxidation/reduction proceeds primarily *via* the upper pathways in the Scheme

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