Electrochemistry of the $[Cu(Hdpa)_2]^{2+/+}$ Couple (Hdpa = di-2-pyridylamine)

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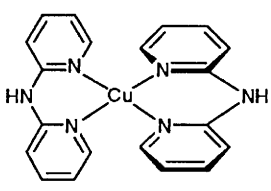
The redox potential of the $[Cu(Hdpa)_2]^{2+/+}$ couple (Hdpa = di-2-pyridylamine) has been determined and the associated structural changes correlated with the kinetic parameters for the copper(II)/copper(I) electron transfer. In accordance with the prediction that one-electron reduction of copper(II) complexes of unusual tetrahedral geometry to the corresponding, usually tetrahedral, copper(I) congeners is thermodynamically favoured, the $[Cu(Hdpa)_2]^{2+/+}$ reduction occurs, in poorly co-ordinating nitromethane solution, at $E^{\circ\prime} = +0.19$ V (*vs.* saturated calomel electrode).

We are interested in determining qualitative relationships between electrochemical parameters and structural reorganizations accompanying electron removal/addition processes in mononuclear[1-3] as well as in metal cluster complexes.[4-7] Special attention has been devoted to copper complexes.[1,2]

The recent X-ray characterization of the copper(I) complex $[Cu(Hdpa)_2]^+$ (Hdpa = di-2-pyridylamine),[8] allowing structural comparison with the long-known copper(II) congener $[Cu(Hdpa)_2]^{2+}$,[9] prompted us to study the electrochemical characteristics of the copper(II)–copper(I) redox change. From the structural viewpoint, in both complexes the copper centre presents a distorted tetrahedral CuN_4 co-ordination; in particular, on passing from the copper(II) to the copper(I) oxidation state the Cu–N bond length increases by about 0.06 Å (from 1.96 to 2.02 Å, on the average) and the dihedral angle between the two CuN_2 ligand planes becomes closer to the value of 90° expected for a perfect tetrahedral geometry (from 55.6 to 73.3°).[8,9] From the electrochemical viewpoint, the copper(II) to copper(I) reduction in a (pseudo)tetrahedral environment is expected to occur at quite positive potential,[10] as well as through an electron-transfer step whose degree of departure from electrochemical reversibility depends upon the induced stereodynamic strain.[11]

Results and Discussion

Fig. 1 shows the cyclic voltammetric features exhibited by $[Cu(Hdpa)_2]^{2+}$, in dimethyl sulphoxide (Dmso) solution. The complex exhibits two subsequent cathodic processes, peaks A and B, respectively. Controlled-potential coulometry indicates that each step involves the addition of one electron per molecule. As illustrated in Fig. 1(*b*), the first reduction displays a directly associated response in the reverse scan (peak E), whereas the second step lacks any directly associated signal, except for the reoxidation peaks C and D which are located at higher potentials. The sharpness of peak C is clearly due to anodic stripping of the copper metal electrodeposited on the platinum electrode after traversing the peak B; the so-generated Cu^+ ion is further oxidized to Cu^{2+} at peak D.



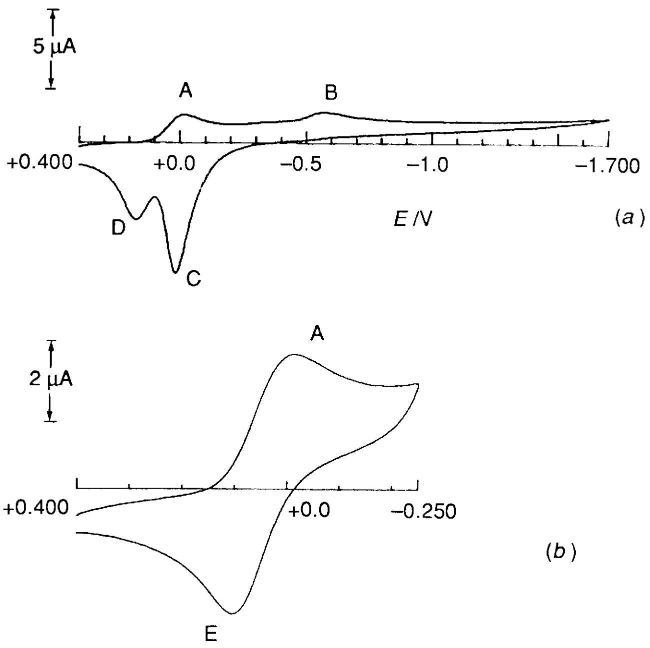


Fig. 1 Cyclic voltammograms recorded at a platinum electrode for a dmso solution containing $[Cu(Hdpa)_2][ClO_4]_2$ (1.20×10^{-3} mol dm^{-3}) and NEt_4ClO_4 (0.2 mol dm^{-3}). Scan rates: (*a*) 0.02 and (*b*) 0.1 V s^{-1}

Analysis[12] of the cyclic voltammetric response exhibited by the copper(II)–copper(I) peak system A/E with scan rate v varying from 0.02 to 2.00 V s^{-1} shows that: (*i*) the $i_{p(E)}/i_{p(A)}$ ratio is constantly equal to the unity; (*ii*) the current function $i_{p(A)}v^{-\frac{1}{2}}$ remains constant; (*iii*) the peak-to-peak separation $[\Delta E_p = E_{p(E)} - E_{p(A)}]$ progressively increases from 98 to 242 mV. All these parameters are diagnostic for a simple one-electron reduction, quasi-reversible in character. The increase in ΔE_p with scan rate can be taken as an index of the departure from pure electrochemical reversibility of the reduction process, when compared with the constant value of 59 mV theoretically expected for a reversible one-electron transfer.[12] Indeed, as reported in Table 1, it is more convenient from an experimental viewpoint to compare this trend in ΔE_p with the corresponding one exhibited by the commonly assumed reversible $[Fe(C_5H_5)_2]^{0/+}$ oxidation, under the same experimental conditions.

By assuming that the slowing of the electron transfer is

Table 1 Comparison of the peak-to-peak separations exhibited by the $[Cu(Hdpa)_2]^{2+/+}$ and $[Fe(C_5H_5)_2]^{0/+}$ couples in dmso solutions containing NEt_4ClO_4 (0.2 mol dm^{-3}) as supporting electrolyte at a platinum working electrode

	ΔE_p/mV	
v/V s^{-1}	$[Cu(Hdpa)_2]^{2+/+}$ ($E^{\circ\prime} = +0.04$ V)	$[Fe(C_5H_5)_2]^{0/+}$ ($E^{\circ\prime} = +0.40$ V)
0.02	98	83
0.05	102	84
0.10	113	88
0.20	131	103
0.50	160	137
1.00	213	172
2.00	242	201

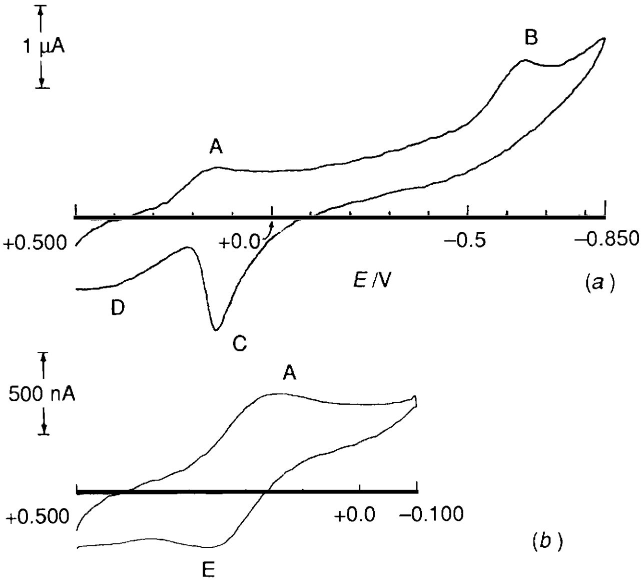


Fig. 2 Cyclic voltammograms recorded at a platinum electrode for a $MeNO_2$ solution saturated with $[Cu(Hdpa)_2][ClO_4]_2$; supporting electrolyte NBu_4ClO_4 (0.2 mol dm^{-3}) Scan rates: (*a*) 0.01 and (*b*) 0.02 V s^{-1}

mainly dominated by the barrier to structural rearrangements rather than solvation effects, one can conclude that the reorganization barrier experienced by the addition of one electron to $[Cu(Hdpa)_2]^{2+}$ is somewhat higher than that experienced by the removal of one electron from $[Fe(C_5H_5)_2]$. Unfortunately, such a conclusion is hardly correlatable with the previously outlined geometrical rearrangements within the tetrahedral CuN_4 co-ordination. Under our experimental conditions, the dmso solutions of $[Cu(Hdpa)_2]^{2+}$ are pale green; this is indicative of the occurrence of solvation to six-co-ordinate species,[13] as structurally confirmed in the case of $[Cu(tpa)_2(MeCN)_2]^{2+}$ (tpa = tri-2-pyridylamine).[14] Finally, dmso solutions of $[Cu(Hdpa)_2]^+$ obtained by exhaustive one-electron reduction ($E_w = -0.2$ V) are lemon-yellow.

A similar redox pattern is exhibited by pale green dimethylformamide (dmf) solutions of $[Cu(Hdpa)_2][ClO_4]_2$ {$E^{\circ\prime}$ for $[Cu(Hdpa)_2]^{2+/+} = +0.16$ V; ΔE_p at 0.2 V s^{-1} = 165 mV}.

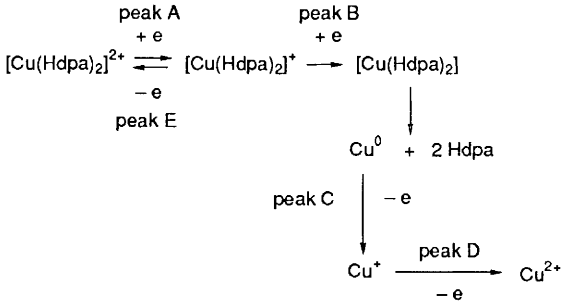
Finally, although $[Cu(Hdpa)_2][ClO_4]_2$ is only very slightly soluble in acetonitrile (MeCN) solution containing NEt_4ClO_4 (0.2 mol dm^{-3}), a pale dirty-yellow solution forms which displays a voltammetric picture similar to those previously described {$E^{\circ\prime}$ for $[Cu(Hdpa)_2]^{2+/+} = +0.27$ V; ΔE_p at 0.2 V s^{-1} = 130 mV}.

Conceivably, the actual copper(II)–copper(I) redox change in co-ordinating solvents is accompanied by a stereodynamic conversion from a tetragonally distorted (likely octahedral, with a planar CuN_4 assembly)[15] to a tetrahedral geometry.

Table 2 Electrochemical characteristics of the $[Cu(Hdpa)_2]^{2+/+}$ and $[Fe(C_5H_5)_2]^{0/+}$ couples at a platinum electrode in $MeNO_2$ solutions containing NBu_4ClO_4 (0.2 mol dm^{-3}) as supporting electrolyte

	ΔE_p/mV	
v/V s^{-1}	$[Cu(Hdpa)_2]^{2+/+}$ ($E^{\circ\prime} = +0.19$ V)	$[Fe(C_5H_5)_2]^{0/+}$ ($E^{\circ\prime} = +0.30$ V)
0.02	120	82
0.05	127	84
0.10	135	86
0.20	145	90

Solvent	$E^{\circ\prime}$/V	E_p/V
$MeNO_2$	+ 0.19	− 0.58
dmso	+ 0.04	− 0.65
dmf	+ 0.16	− 0.54
MeCN	+ 0.27	− 0.44



Scheme 1

More problematic is to define the electrochemistry of the $[Cu(Hdpa)_2]^{2+/+}$ redox change in poorly co-ordinating solvents, in that $[Cu(Hdpa)_2][ClO_4]_2$ is completely insoluble both in dichloromethane and tetrahydrofuran solutions [containing NBu_4ClO_4 (0.2 mol dm^{-3}) supporting electrolyte]. Nevertheless, in contrast to the fact that nitromethane ($MeNO_2$) solutions of $[Cu(Hdpa)_2]^{2+}$ have been reported to be green in colour,[13] we found that $[Cu(Hdpa)_2][ClO_4]_2$ is only very slightly soluble in nitromethane solutions containing NBu_4ClO_4 supporting electrolyte, producing a faint pink colour, which is probably indicative that the tetrahedral co-ordination of the copper(II) centre persists in solution.[16] Fig. 2 shows the cyclic voltammetric behaviour exhibited by such a solution. Comparison with Fig. 1 shows that a qualitatively similar reduction pathway holds, which can be hence depicted as in Scheme 1.

Controlled-potential electrolysis ($E_w = -0.2$ V) produces a lemon-yellow solution of the copper(I) complex $[Cu(Hdpa)_2]^+$. Subsequent reoxidation ($E_w = +0.4$ V) precipitates $[Cu(Hdpa)_2][ClO_4]_2$.

In order to evaluate the kinetic aspect of the copper(II)–copper(I) electron transfer, Table 2 illustrates the trend of ΔE_p with scan rate. It seems that the geometrical reorganization towards a more tetrahedral CuN_4 assembly, demonstrated in the solid state and likely accompanying the $[Cu(Hdpa)_2]^{2+/+}$ redox change in non-co-ordinating solvents, involves an energy barrier higher than that operative in the $[Fe(C_5H_5)_2]^{0/+}$ oxidation, which involves a reorientation of the cyclopentadienyl rings from a staggered (or, at least, from a random distribution of staggered and eclipsed conformations) to an eclipsed conformation together with an elongation of about 0.4 Å in the iron ring centre distance (on average from 1.66 to 1.70 Å).[17–19] In addition, in agreement with the theoretical prediction, the redox potential for the copper(II)–copper(I) reduction occurs at potentials which are among the highest

Table 3 Formal electrode potentials {*vs.* $[Fe(C_5H_5)_2]^{0/+}$} for the copper(II)–copper(I) redox change in different CuN_4 complexes

Couple	$E^{\circ\prime}/V$	Solvent	Ref.
$[Cu(Hdpa)_2]^{2+/+}$	-0.36	dmso	Present work
	-0.29	dmf	Present work
	-0.11	MeCN	Present work
	-0.11	$MeNO_2$	Present work
$[Cu(bipy)_2]^{2+/+}$	-0.50	Me_2CO	20
$[Cu(phen)_2]^{2+/+}$	-0.58	dmf	21

recorded for CuN_4 complexes.[2] In particular, a direct comparison with $[Cu(bipy)_2]^{2+}$ (bipy = 2,2′-bipyridyl) and $[Cu(phen)_2]^{2+}$ (phen = 1,10-phenanthroline), which possess a pseudo-tetrahedral CuN_4 co-ordination, seems pertinent.

In order to confirm the easiest access to copper(I) from a comparison among electrochemical data from different solvents, Table 3 summarizes the copper(II)–copper(I) electrode potentials with reference to the $[Fe(C_5H_5)_2]^{0/+}$ couple, bearing in mind the common extrathermodynamic assumption that its redox potential is independent of the solvent.[22] It seems evident that beyond the geometry imposed on the copper(II) ion by the co-ordinating properties of the solvent, the electronic properties of the Hdpa ligand favour the one-electron reduction to an extent higher than do those of bipy and phen.

Experimental

The complex $[Cu(hdpa)_2][ClO_4]_2$ was prepared according to published procedures.[9,16]

The materials and apparatus for electrochemistry have been described elsewhere.[3] Unless otherwise specified the potentials are referred to the aqueous calomel electrode (SCE).

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Received 13th May 1991; Paper 1/02261J