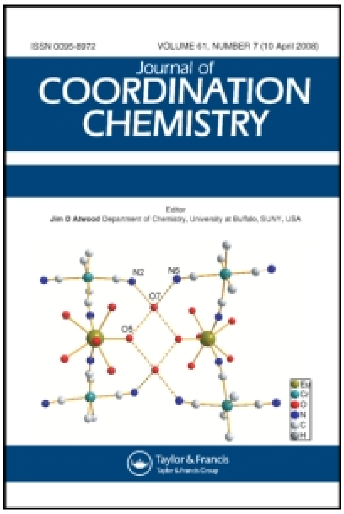

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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF TETRANUCLEAR COPPER(I) COMPLEX CONTAINING 3-(PYRROL-1-YLMETHYL)PYRIDINE AS LIGAND

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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF TETRANUCLEAR COPPER(I) COMPLEX CONTAINING 3-(PYRROL-1-YLMETHYL)PYRIDINE AS LIGAND

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The crystal structure of the tetranuclear complex [(pmp)CuI]$_4$, where pmpy = 3-(pyrrol-1-ylmethyl)pyridine), [$Cu_4I_4C_{40}H_{40}N_8$] (I) has been determined. (I) crystallizes in the triclinic system, space group p –1, with a = 13.008(3), b = 14.047(3), c = 14.392(3) Å, α = 68.80(2), β = 80.83(2), γ = 72.62(2)° and two formula units per unit cell. Refinement by full-matrix least-squares gave final residuals of R = 0.0602 and Rw = 0.0552. Results from NMR spectroscopy show that pmp coordinates only through its pyridine nitrogen atom. The Cu_4I_4 core has a distorted "cubane-like" arrangement with Cu-I distances ranging from 2.644(1) to 2.764(1) Å. Data from nuclear magnetic resonance, electronic spectra and cyclic voltammetry are presented and discussed.

Keywords: crystal structures; copper and iodine complexes, cluster-polypyrrole film.

INTRODUCTION

In view of the remarkable ability of octanulcear copper and iodine clusters to photoinduce electron transfer,[1–2] and their ability to bind dioxygen,[3] we chose to synthesize a complex with the pyridine ligand

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covalently bonded to the terminal pyrrole subunit, consistent with their tendency toward electropolymerization. Electropolymerization of pyrrol in acetonitrile generates an electroactive polypyrrole film for use in redox photocatalysis. Studies of polypyrrolic films are moving to new materials with the new chemically functionalized groups that add new properties to the films such as redox catalysis, electrochromism and asymmetrical recognition with applications in areas such as electrochromic windows, fuel cells, batteries and electrochemical sensors. To achieve this goal, several examples of transition metal complexes coordinated to the starting monomer prior to electropolymerization have been described.[4] In this work, a new monomeric unit formed by an octanulcear copper (I) and iodine containing-3-(pyrrol-l-ylmethyl)pyridine as a ligand is presented along with the results of NMR, electronic spectra, and infrared spectra. It was of interest to determine the structure of the crystalline form of $[(pmp)CuI]_4$, and to see how much it differs from the crystal structure of analogous $[(L)CuX]_4$ complexes with different ligands. Also reported are preliminary redox studies.

EXPERIMENTAL

Materials

The ligand pmp was purchased from Aldrich and was used without further purification. All other reagents were of the highest purity available from commercial sources and were used without further purification. Cuprous iodide (CuI) was prepared by following the literature methods with minor modifications.[5] Stoichiometric amounts of 1:1 copper sulphate and KI were dissolved in water. The by-product of this reaction is (I_2), which can be removed with organic solvents or by passing SO_2 through the solution. However, if the reaction medium is kept warm (70 to 80°C) most of the I_2 sublimes and the product can be collected free of iodine. The remaining product was then washed with chloroform $(CHCl_3)$ and dried with a small amount of ether.

Synthesis of $[(pmp)CuI]_4$

CuI was dissolved in a saturated solution of KI, because it is only slightly soluble in water. An ethanolic solution of pmp was added to the aqueous solution of CuI. The product readily precipitated, giving a white, air-stable solid. Single crystals were obtained by redissolving the solid in acetone. The elemental CHN analysis confirms the purity of the expected compound. Experimental(%) (Calculated(%)): 34.42(34.42); 2.71(2.87); 8.01(8.03).

X-ray Diffraction Study

A white block of dimensions 0.25 × 0.55 × 0.65 mm was mounted on a glass fiber and centered on a CAD4 diffractometer. Determination of the crystal class, orientation matrix, and unit cell dimensions was performed in standard fashion using the CAD4-Express program.[6] Least-squares refinement of 25 automatically centered reflections gave the cell constants reported in Table 1. Intensity data for the complex were reduced using the MOLEN software.[7] The structure was solved using the program

TABLE I Crystal data and details of the structure determinations of $[(pmp)CuI]_4$

Formula	$Cu_4I_4C_{40}H_{40}N_8$
Formula weight	1394.6
Space group	P-1 (No. 2)
Cell constants	
a (Å)	13.008(3)
b (Å)	14.047(4)
c (Å)	14.392(3)
α (°)	68.80(2)
β (°)	80.83(2)
γ (°)	72.61(2)
Volume (Å^3)	2335.7(9)
z	2
D_{calc}(g/cm^3)	1.983
T (K)	296
Radiation	Mo Rα (0.71073 Å)
μ (cm^{-1})	44.6
F(000)	1328
Range of data collection, θ(°)	2.1–25
Scan technique	θ–2θ
h, k, l range	-14, 15/0, 16/ -15, 17
[(sin θ) /λ]max (Å^{-1})	0.5940
Measured reflections	8549
Unique data	8186
Data used	6403
criterion	$I>3\sigma I$
Absorption correction Empirical,	ψ scan
T_{max}, T_{min}	0.9994, 0.6384
Function minimized	$\Sigma w(\lvert Fobs \rvert - \lvert Fcalc \rvert)^2$
Weighting scheme	$w = 1/[\sigma^2 (Fobs)]$
R, R_w	0.0602, 0.0552
No. parameters	446
Obs./parameter	14.3
Max. shift/error	0.46

SIR92.[8] An empirical ψ — scan absorption correction was applied.[9] Full-matrix least-squares refinement was executed for non-hydrogen atoms with anisotropic thermal parameters except for the C3 and C4 carbon atoms, and groups N31’-C35’ and N41’-C45’, for which isotropic thermal parameters were employed. These atoms seem to have thermal parameters too large for meaningful anisotropic refinement. This is reflected in the larger deviations of the structural parameters of the groups from standards values. The hydrogen atoms were placed at their calculated positions with fixed temperature factors of 6.0 Å^2.

Atomic coordinates for the non-hydrogen atoms are listed in Table 2. Atomic scattering factors were taken from the International Tables for X-ray Crystallography. The molecular illustration was drawn with

TABLE 2 Final atomic positional parameters and equivalent isotropic temperature factors for $[(pmp)CuI]_4$ with e.s.d. in parentheses

Atom	*x/a*	*y/b*	*z/c*	*B(Å^2)*
I1	0.17888(5)	0.26403(4)	0.91626(4)	5.39(1)
I2	0.34776(4)	0.38198(4)	0.61735(4)	4.87(1)
I3	0.47013(5)	0.04648(4)	0.81681(4)	4.95(1)
I4	0.16229(4)	0.13789(4)	0.67167(4)	4.90(1)
Cu1	0.35407(9)	0.17607(9)	0.65930(8)	5.31(3)
Cu2	0.25482(9)	0.10201(9)	0.84173(8)	5.64(3)
Cu3	0.17680(9)	0.30100(9)	0.71839(9)	5.60(3)
Cu4	0.36381(9)	0.25231(8)	0.80403(8)	5.50(3)
N11	0.4379(5)	0.1540(5)	0.5333(5)	4.6(2)
N21	0.1992(6)	-0.0131(5)	0.9545(5)	5.0(2)
N31	0.0535(5)	0.4320(5)	0.6752(5)	5.2(2)
N41	0.4655(5)	0.2892(5)	0.8718(5)	5.0(2)
N11′	0.7382(6)	0.2417(6)	0.3236(5)	5.6(2)
N21′	0.2050(8)	-0.1812(6)	1.3063(6)	7.1(2)
N31′	-0.0784(7)	0.7939(7)	0.6751(6)	7.0(2)*
N41′	0.7013(8)	0.5062(7)	0.8523(7)	7.8(2)*
C1	0.7176(7)	0.1647(7)	0.4200(7)	5.7(2)
C2	0.160(1)	-0.0779(8)	1.2331(8)	11.3(5)
C3	0.007(2)	0.701(2)	0.688(2)	19.3(9)*
C4	0.617(2)	0.495(2)	0.802(2)	15.7(7)*
C12	0.5402(7)	0.1644(6)	0.5166(6)	4.8(2)
C13	0.6023(7)	0.1559(6)	0.4317(6)	5.0(2)
C14	0.5591(8)	0.1361(8)	0.3598(7)	6.5(3)
C15	0.4535(8)	0.1268(8)	0.3764(7)	6.9(3)
C16	0.3951(8)	0.1367(7)	0.4642(7)	5.8(2)
C12′	0.795(1)	0.2151(8)	0.2435(8)	7.9(3)
C13′	0.788(1)	0.311(1)	0.1647(9)	8.8(4)
C14′	0.7297(9)	0.3936(9)	0.2006(9)	7.8(3)
C15′	0.7003(9)	0.3489(8)	0.2994(8)	6.8(3)
C22	0.2071(9)	-0.0214(7)	1.0487(6)	6.2(3)

TABLE 2 *(cont'd)*

Atom	*x/a*	*y/b*	*z/c*	*B(Å²)*
C23	0.159(1)	-0.0858(7)	1.1298(7)	6.7(3)
C24	0.1016(9)	-0.1469(7)	1.1138(8)	6.8(3)
C25	0.0948(8)	-0.1402(7)	1.0168(7)	6.3(3)
C26	0.1431(7)	-0.0709(6)	0.9381(7)	5.3(2)
C22′	0.312(1)	-0.2401(9)	1.3142(9)	9.0(3)
C23′	0.3161(9)	-0.328(1)	1.3966(9)	8.0(4)
C24′	0.2139(8)	-0.3224(8)	1.4408(7)	6.6(3)
C25′	0.1460(7)	-0.2307(8)	1.3864(7)	6.4(3)
C32	0.0595(8)	0.5170(7)	0.6925(9)	7.4(3)
C33	-0.0173(9)	0.6117(8)	0.666(1)	10.2(4)
C34	-0.1055(9)	0.6222(8)	0.6153(9)	7.3(3)
C35	-0.1137(8)	0.5343(8)	0.5972(7)	6.4(3)
C36	-0.0314(7)	0.4404(7)	0.6275(6)	5.5(2)
C32’	-0.144(2)	0.778(2)	0.757(2)	16.7(8)*
C33’	-0.222(2)	0.862(1)	0.737(1)	14.5(6)*
C34’	-0.204(1)	0.934(1)	0.642(1)	8.7(3)*
C35’	-0.107(2)	0.912(2)	0.588(2)	15.1(7)*
C42	0.5060(8)	0.3712(7)	0.8260(8)	6.4(3)
C43	0.5789(9)	0.3943(9)	0.8698(9)	9.8(3)
C44	0.6087(9)	0.3324(9)	0.9654(8)	7.7(3)
C45	0.5652(8)	0.2459(8)	1.0151(7)	6.4(3)
C46	0.4941(7)	0.2271(7)	0.9650(7)	5.7(2)
C42′	0.700(1)	0.572(1)	0.916(1)	10.5(4)*
C43′	0.806(1)	0.533(1)	0.939(1)	9.2(3)*
C44′	0.860(1)	0.461(1)	0.901(1)	12.2(5)*
C45′	0.802(1)	0.446(1)	0.853(1)	10.0(4)*

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma) *B(1,2) + ac(cos beta) *B(1,3) + bc(cos alpha)*B(2,3)]

ORTEP.[11] All calculations were performed on a DEC 3000 AXP computer.

Physical Measurements

The electronic spectra were obtained with a Hewlett Packard spectrophotometer model HP8452A. The infra-red spectra were recorded on a Perkin-Elmer model 1GPC FT-IR (and far infra-red) ^{1}H NMR spectra were recorded with a Brucker AC200F in CD_3Cl. The elemental analyses were performed on a Perkin-Elmer CHN analyzer model 2400. The cyclic voltammetry setup used in this work has been described previously.[12] All potentials are quoted with respect to the normal hydrogen electrode (NHE).

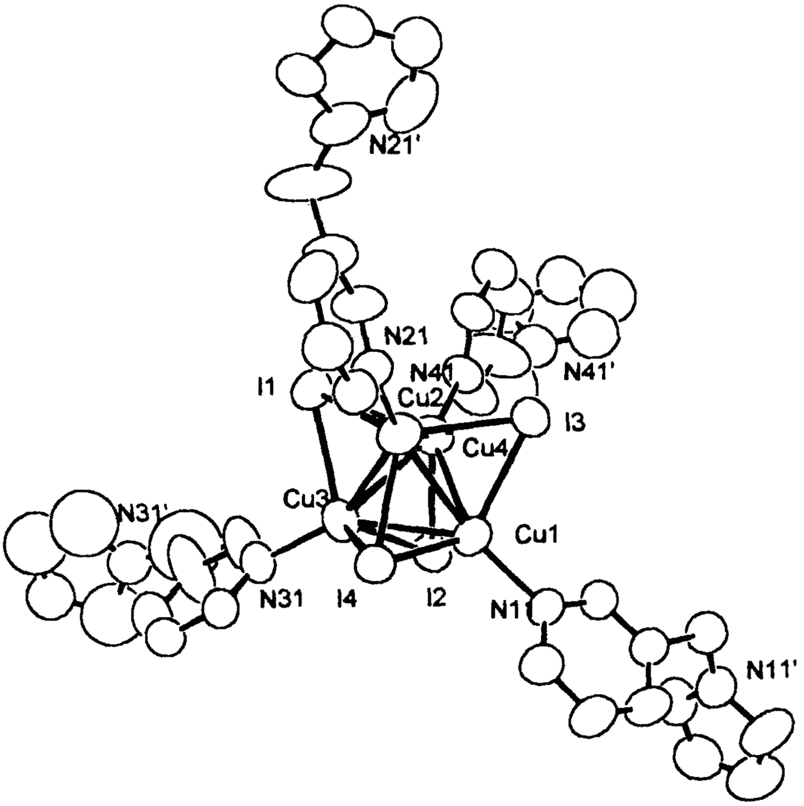

FIGURE 1 Perspective view of the molecule with labeling of essential atoms. The displacement ellipsoids are drawn at the 50% probability level.

RESULTS AND DISCUSSION

Structure of the Copper-Iodine Cluster

Figure 1 shows the scheme for atoms in the cluster. Intramolecular distances and angles are displayed in Tables 3 and 4. The tetrahedrally-distorted cubane shows an arrangement where each d^{10} Cu(I) ion is linked to three μ_3-iodides and a terminal pmp ligand. The pmp ligand is bonded to copper by the nitrogen atom on the pyridine ring (Cu-N pyridine distances range from 2.037(7) to 2.049(6) Å) with average 2.043(6) Å as compared to 2.042(2)Å in $[(py)CuI]_4$[13] and 2.036(7) Å in $[(DENC)CuI]_4$[3] (DENC = N, N-diethylnicotinamide). The six nonbonding Cu...Cu distances range from 2.675(2) to 2.735(2) Å, with average value of 2.703(21) Å which is comparable to 2.690(5) Å for [(py)CuI]$_4$[13]and shorter than the 2.927(20)Å found in [(PEt$_3$)CuI]$_4$, the 2.930(78) Å found in [(PMePh$_3$)CuI]$_4$, the 2.7826 (24) Å in [(AsEt$_3$)CuI]$_4$[14] and the 2.834(51) Å in [(PMePh$_3$)CuI]$_4$.[15] The iodine...iodine contacts range from 4.438(9) to 4.538(8) Å, with average 4.498(37) Å. These values differ slightly from the values reported earlier, 4.4525(15) Å in [(AsEt$_3$)CuI]$_4$, 4.3800(11) Å in [(PEt$_3$)CuI]$_4$[14] and 4.497(36) Å in [cu(DENC)$_4$I$_4$].[3] It is well known that distortions from a regular cubane-like geometry are due to the six iodine...iodine contacts. In addition a decrease in the Cu-I-Cu angle was reported to be due to the contacts. In addition a decrease in the Cu–I–Cu angle was reported to be owing to the repulsion between the iodide atoms.[3] The observed values are between 58.49(3) and 60.98(3)° as compared with the internal angle of 90° for the cubane-like geometry. The 12 Cu-I(μ_3) bond lengths range from 2.644(1) to 2.764(1) Å, with an average value of 2.699(37) Å as compared to 2.695(42) Å in [(DENC)CuI]$_4$,[3] 2.6767(15) Å in [(AsEt$_3$)CuI]$_4$,[14] 2.6837 (13) Å in [(PEt$_3$)CuI]$_4$,[14] 2.698(58) Å in [(PMePh$_3$)CuI]$_4$[16] and 2.688(17) Å in [(AsPh$_3$)CuI]$_4$.[16] There is no marked difference between the structure

TABLE 3 Important distances (Å) between atoms for [(pmp)CuI]$_4$

		(A) Copper...Copper Distances			
Cu1	Cu2	2.718(1)	Cu2	Cu3	2.699(1)
Cu1	Cu3	2.675(2)	Cu2	Cu4	2.735(2)
Cu1	Cu4	2.698(2)	Cu3	Cu4	2.694(2)
av[a]	Cu....Cu	2.703(21)			
		(B) Iodine...Iodine Distances			
I1	I2	4.4814(8)	I2	I3	4.4918(8)
I1	I3	4.5009(9)	I2	I4	4.5387(8)
I1	I4	4.5339(8)	I3	I4	4.4388(9)
av[a]	I....I	4.498(37)			
		(C) Copper-Iodine Distances			
I1	Cu2	2.719(1)	I3	Cu1	2.682(1)
I1	Cu3	2.707(1)	I3	Cu2	2.675(1)
I1	Cu4	2.672(1)	I3	Cu4	2.759(1)
I2	Cu1	2.711(1)	I4	Cu1	2.670(1)
I2	Cu3	2.764(1)	I4	Cu2	2.716(1)
I2	Cu4	2.644(1)	I4	Cu3	2.674(2)
av[a]	I-Cu	2.699(37)			
		(D) Copper-Nitrogen distances			
Cu1	N11	2.037(7)	Cu2	N21	2.049(6)
Cu2	N21	2.049(6)	Cu4	N41	2.039(9)
av[a]	Cu-N	2.043(6)			

[a] Errors on average distances are calculated by $\sigma(\mathrm{av}) = [\Sigma_i(d_i-d_a)^2/(N-1)]^{1/2}$, where d_i is the *i*th distance and d_a is the average of N (such a distance is a measure of the precision of the value.)

TABLE 4 Selected intramolecular angles (deg), for $[(pmp)CuI]_4$

			(A)Cu_4I_4 "Cube" Angles				
Cu2	I1	Cu3	59.66(3)	I2	Cu1	I3	112.77(5)
Cu2	I1	Cu4	60.96(4)	I2	Cu1	I4	114.98(4)
Cu3	I1	Cu4	60.10(4)	I3	Cu1	I4	112.02(4)
Cu1	I2	Cu3	58.49(3)	I1	Cu2	I3	113.10(6)
Cu1	I2	Cu4	60.50(4)	I1	Cu2	I4	113.10(4)
Cu3	I2	Cu4	59.70(4)	I3	Cu2	I4	110.82(4)
Cu1	I3	Cu2	60.98(3)	I1	Cu3	I2	110.01(5)
Cu1	I3	Cu4	59.43(4)	I2	Cu3	I4	113.11(5)
Cu2	I3	Cu4	60.40(4)	I1	Cu3	I4	114.85(4)
Cu1	I4	Cu2	60.61(4)	I1	Cu4	I2	114.92(4)
Cu1	I4	Cu3	60.06(4)	I1	Cu4	I3	111.91(4)
Cu2	I4	Cu3	60.09(4)	I2	Cu4	I3	112.43(5)
av^a	Cu-I-Cu		60.08(7)	av^a	I-Cu-I		112.8(1.6)
			(B)Nitrogen-Copper-Iodine Angles				
I2	Cu1	N11	98.9(2)	I1	Cu3	N31	103.0(2)
I3	Cu1	N11	108.5(2)	I2	Cu3	N31	100.0(2)
I4	Cu1	N11	108.6(2)	I4	Cu3	N31	114.6(3)
I1	Cu2	N21	99.4(2)	I1	Cu4	N41	106.0(3)
I3	Cu2	N21	111.5(2)	I2	Cu4	N41	108.7(2)
I4	Cu2	N21	108.3(2)	I2	Cu4	N41	108.7(2)
av^a	I-Cu-N		105.8(5.1)				
			(C)Copper-Nitrogen-Carbon Angles				
Cu1	N11	C12	117.4(6)	Cu3	N31	C32	116.9(6)
Cu1	N11	C16	123.5(6)	Cu3	N31	C36	124.9(7)
Cu2	N21	C22	118.4(7)	Cu4	N41	C42	121.7(6)
Cu2	N21	C26	122.8(6)	Cu4	N41	C46	119.3(7)
av^a	Cu-N-C		120.6(3.0)				

[a] see footnote of Table 3.

of $[(pmpy)CuI]_4$ and the previously reported structures of $[(py)CuI]_4$[13] and $[(DENC)CuI]_4$.[3]

Spectroscopy and Luminescence

Electronic spectra exhibit only charge-transfer (CT) maxima in the ultraviolet region. Copper and iodine with the pmp ligands show luminescent features in solution and in the solid state, that may be applicable to studies involving electrophotolysis.[13] Crystals of $[(pmp)CuI]_4$ show an intense emission band at 710 nm and a second emission band at 480nm. Earlier studies have shown photoluminescence of analogous clusters at room temperature in the solid state. Emission of intense yellow light from solid samples of the $[(pmp)CuI]_4$ can also be observed by visual inspection when samples are irradiated by uv light. Emission spectra of 10^{-3} M $[(pmp)CuI]_4$ in acetone show two emission bands, a low intensity band at 450nm and a high intensity band at 740nm, upon excitation by 370 nm radiation. Ford and Vogler[1–2,17] reported emission of visible light for similar clusters and assigned these bands to halogen to metal charge transfer (XMCT) and to halogen to ligand charge transfer (XLCT). The XLCT low energy emissions are reported only for clusters with Cu-Cu distances ($d_{Cu\text{-}Cu}$) less than the sum of the Cu(I) van der Waals radii (2.8Å). The Cu-Cu distance found in [(pmp)CuI]$_4$ complex contrasts, $d_{Cu\text{-}Cu}$ values exceeding 3.0Å typical for analogous chloride clusters.[2] The packing of the small chlorides tend to give larger Cu$_4$ tetrahedra with less Cu-Cu interaction. It seems from this work, that packing in Cu$_4$X$_4$ is not influenced by the pmp ligand. Life time determinations are underway to explore the luminescent features of this cluster.

^{1}H NMR Spectra

The ^{1}H NMR spectra for pmp and [(pmp)CuI]$_4$ in CDCl$_3$ are shown in Figure 2 and the values for resonance peaks in both the ligand and the cluster are displayed in Table 5. Resonances associated with the protons a, a' and bc from the pyridine ring of pmp, were affected by coordination. The peak at 8.4 ppm is slightly shifted to 8.8 ppm and broadened relative to the a, a' peak of the pmp. The same shift was observed in similar clusters of copper-halogen, coordinated with pyridinic ligands.[3] Taube[18]

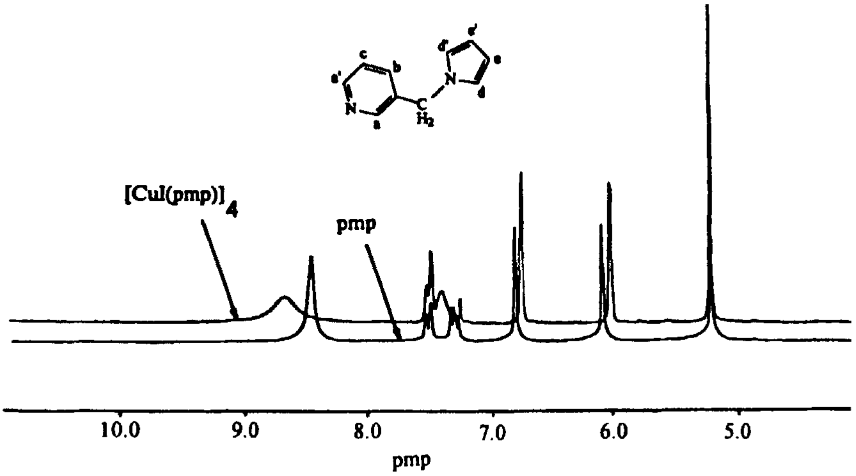

FIGURE 2 ^{1}H NMR spectra of pmp and [(pmp)CuI]$_4$ in CDCl$_3$ at 25°C with tetramethylsilane as reference.

TABLE 5 ^{1}H NMR chemical shift for pmp and [(pmp)CuI]$_4$

^{1}H assigned	*pmp*	*[(pmp)CuI]$_4$*	*Protons type*
a,a'	8,4	8,8	2^{1}H broad
b,c	7,5–7,2	7,6–7,4	2^{1}H broad
d,d'	6,8	6,8	2^{1}H doublet
e,e'	6,1	6,1	2^{1}H doublet
CH_2	5,2	5,3	2^{1}H doublet

found the same ^{1}H NMR shift in ligands having protons close to the metallic center in complexes coordinated with halogens.

Electrochemistry

Preliminary cyclic voltametric studies show the clusters are electroactive and their electrochemical behaviour depends on parameters such as the potential scan rate and the molar concentration of the compound. Reproducibility of these cyclic voltammetric experiments was obtained by absolute cleanness of the Pt electrode surface. A typical voltammogram (Fig. 3) obtained in acetonitrile in the potential range of 0.1 to 1.40 V *vs* the NHE exhibit six peaks; three anodic and three cathodic peaks. Scanning positively at a scan rate of 40mV/s, a first wave is observed at 0.58 V, an intense anodic peak is found at 0.92 V and one less intense peak is found at 1.3 V. Ford and colleagues[19] found values of ~+0.63 and ~+0.80 V *vs.* Ag/AgCl for $Cu_4I_4py_4$ and no cathodic peak was found. The number of electrons transferred was not determined but according to Ford *et al.*[19] the peak at 0.58V is the result of a cluster species formed by ligand dissociation and the wave at 0.92V can be associated with oxidation of $Cu_4I_4py_4$. The cathodic peak at 0.73V is associated with the anodic peak found at 0.92V and is probably due to reduction of $Cu_4I_4pmp_4$. The magnitude of this reduction peak does not diminish although the other peaks diminished in magnitude after several scans. The peak found at 1.3V is due to oxidation of pmp and is associated with the irreversible cathodic peak found at 1.06V and 0.26V. It is well known from the literature[20-21] that N-substituted pyrrole compounds are oxidized at potentials ranging from 1.0 to 1.3 V. From differential pulse voltammetry (DPV) at a scan rate of 20 mV/s (Fig. 1b) only two intense anodic waves at 0.85 and 0.61 V where found. Extensive electrochemical studies are currently underway to clarify the electrochemical mechanism and permit utilization of this cluster as a copolymer in electropolymerization of pyrrol.

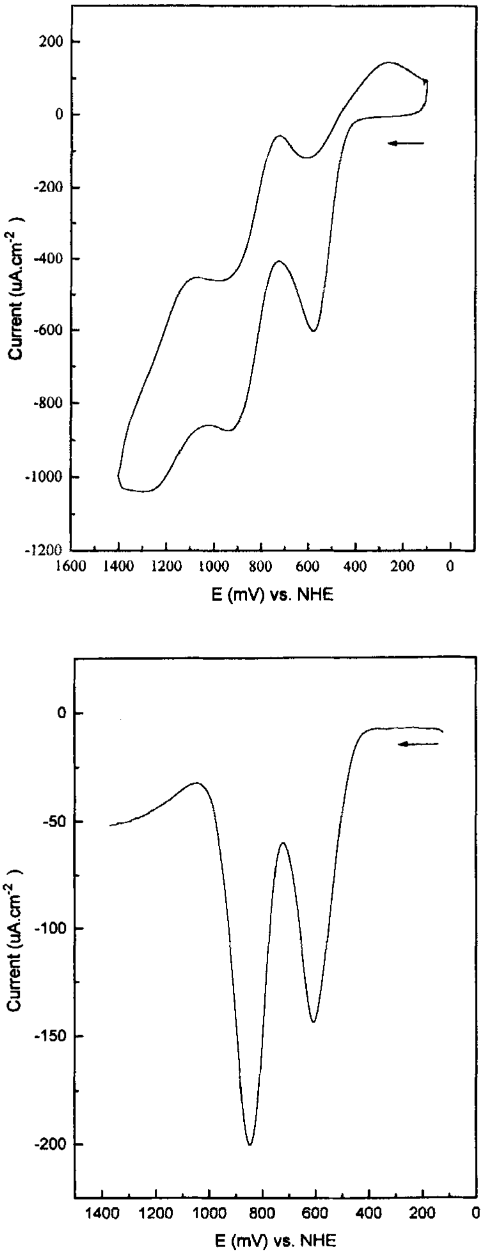

FIGURE 3 (a) Cyclic voltammogram of $[CuI(pmp)]_4$ in Pt at scan rate 40 mV.s^{-1} and (b) Diferencial Pulse Voltammogram at scan rate 10 mV.s^{-1}; pulse width 50ms; pulse height 25 mV. Acetonitrile + 0.1M $TBAPF_6$.

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Supplementary material

A complete lists of bond distances, bond angles, anisotropic thermal parameters, hydrogen coordinates (9 pages) and observed and calculated structure factors (72 pages) are available from the authors.

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