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Activity of oxidative coupling catalysts with carbon disulphide to generate the first new redox dithiocarbonato moiety $[(Pip)_nCuX]_4(CS_2O)_2$

Mohamed A. El-Sayed[1], Ahmed H. Abdel-Salam[1,2*], Hemmat A. El-Badawy[1] and Ali El-Dissouky[1]
[1]Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
[2]Chemistry Department, Faculty of Science, University of Jeddah, Jeddah, Saudi Arabia
ahmedhassan179@yahoo.com

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Abstract

A new series of tetranuclear $[(Pip)_nCuX]_4(CS_2O)_2$, where Pip = Piperidine, n = 1 or 2 X = Cl or Br, are obtained according to the reaction of the lewis acid $[(Pip)_nCuX]_4O_2$ towards the lewis base CS_2 at room temperature. The synthesised compounds are characterized using molecular weight determination, elemental analysis and spectral techniques (FTIR, UV/Vis. and EPR). The FTIR spectral data showed that CS_2O^{2-} group acts as a dibasic bidentate or tridentate bridging ligand for n=2 or 1, respectively. The bridging CS_2O^{2-} containing tetranuclear complexes display a $CS_2O^{2-} – Cu^{2+}$ Charge transfer band at 430-410nm for all $[(Pip)_nCuX]_4(CS_2O)_2$ complexes with molar absorptivity varying from 4000 to $14000M^{-}\ cm^{-1}$. Bidentate bridging anion $(CS_2O)^{2-}$ in $[(Pip)_2CuX]_4(CS_2O)_2$ shows another charge transfer with Cu(II), at 605nm and 575nm with molecular absorptivities 810 and $970M^{-1}cm^{-1}$ for X=Cl and Br respectively. The electrochemical behavior of the new tetranuclear complexes are studied where the dithiocarbonato anion in $[(Pip)_nCuX]_4(CS_2O)_2$ is found to be electrochemically active showing quasi-reversible peaks at a more positive potentials, when compared with Cu(II) centres. The complexes are shown to be catalytically inactive toward the oxidation of 2,6-dimethyl phenol unlike their oxo and carbonato analogues.

Keywords: Dithiocarbonate, Copper(II), 2,6-Dimethylphenol, EPR, Cyclic voltammetry.

Introduction

Reactivity of suitable copper (I) complexes with dioxygen generate industrial catalysts of important biological interest, as they mimic copper protein such as tyrosinase[1-4]. Dioxygen can be reduced to superoxo, μ-peroxo as trans-μ-1,2-peroxo- or μ–η^2: η^2-peroxo-, hydroxo or oxo, depending on; the structure of copper (I) complexes, ligands around copper (I) centres, solvent type, charge on coordination sphere, copper-copper distance and temperature[5-15].

Copper(I) halides react quantitatively with (Pip) in oxygen-free weakly coordinating aprotic solvents such as methylene chloride or nitrobenzene to form tetranuclear complexes $[(Pip)_nCuX]_4$; n = 1 or 2, X = Cl, Br or I, Equations (1,2).

$$4\ Pip + 4\ CuX \rightarrow [(Pip)CuX]_4 \quad (1)$$

$$8\ Pip + 4\ CuX \rightarrow [(Pip)_2CuX]_4 \quad (2)$$

Vokler Schramm[16] was able to study the molecular geometry of the tetrameric molecule $[(Pip)CuI]_4$ using X-ray crystallography and described it as a built up by an inner tetrahedral Cu_4 cluster surrounded by a co-centric and opposed larger I_4 tetrahedron with each I attached to three copper atoms and each piperidine ring bonded via nitrogen, donating its lone pair to one copper atom. It was found, close similarity between the molecular (core) structure of $[(Pip)CuI]_4$ with that previously reported for $[LCuI]_4$; L=N,N-diethylnicotinamide (DENC) or pyridine (Py)[16,17].

In earlier work we reported that copper(I) complexes, $[(Pip)_nCuX]_4$ were oxidized first by dioxygen according to a reaction stoichiometry to form $[(Pip)_nCuX]_4O_2$ and the product complexes rapidly react with CO_2 forming the carbonato complexes $[(Pip)_nCuX]_4(CO_3)_2$[15,18]. This reaction was considered as Lewis acid-base reaction, in which CO_2 worked as a Lewis acid and react with basic μ-oxo Cu(II) centres[15,18,19]. The cryoscopic data indicated that all $[(Pip)_nCuX]_4(CO_3)_2$ complexes, like their copper(I) precursors, were discrete tetranuclear species which have no tendency to disproportionate ,unlike oxidation products of $[L_nCuX]_4$; L=pyridine[20]. Electronic transition spectra with large molecular absorptivity in the near infrared were diagnostic for tetranuclear cuban core structure to attain 3 halo-ligands for each Cu centre in $[(Pip)_n CuX]_4(CO_3)_2$[15,18,19,21]. The room temperature solid state EPR spectra for $[(Pip)_n CuX]_4(CO_3)_2$ were axial type of spectra with $d_{x^2-y^2}$ ground state suggesting elongated tetragonal distortion for all of them. Cyclic voltammograms for $[(Pip)_n CuX]_4(CO_3)_2$ were irreversible in character. These tetranuclear carbonato complexes showed catalytical activity. They initiate the oxidation of 2,6-dimethylphenol (DMP) to 3,3',5,5'-tetramethyl-4,4'-diphenoquinone (DPQ)[15,22-25].

Due to our interest in the synthesis and study the reactivity of the tetra nuclear copper(II) complexes, we aim to study the reactivity of $[(Pip)_n CuX]_4O_2$; n=1 or 2 and X = Cl or Br, Pip = piperidine with CS_2, to i. answer the question, can CS_2 act as Lewis acid with Lewis base μ-oxo centres in $[(Pip)_nCuX]_4O_2$ to form dithiocarbonato moiety like CO_2 which forms the carbonato analogue?, and ii. If the answer is yes, then i. what is the stoichiometry of the reaction?, ii. what is the mode of coordination of dithiocarbonato in the title tetranuclear copper (II) complexes?, iii. is dithiocarbonato moiety redox active in $[(Pip)_nCuX]_4(CS_2O)_2$? And iv. will $[(Pip)_nCuX]_4O_2$ lose its catalytic activity when it reacts with CS_2?

Materials and methods

The complexes were synthesized similar to the carbonato analogue, except that the CO_2 gas is replaced by CS_2[21]. The Stoichiometry of the products was established specrophotometrically by molar ratio method (Figures-1 and 2), the products were then characterized by combining infrared, uv-visible, EPR spectral studies and cyclic voltammetry[26]. Finally, the catalytic activity of the products toward the oxidation of 2,6-dimethylphenol.

Results and discussion

The dithiocarbonato complexes, $[(Pip)_n CuX]_4(CS_2O)_2$, were synthesised by the reaction of $[(Pip)_n CuX]_4O_2$ with CS_2 according to equation 3, their stoichiometries were studied spectrophotometrically by molar ratio method, molecular weight determination and elemental analysis. All complexes are very stable for long time at room temperature and soluble in all aprotic media.

Stoichiometry of $[(Pip)_nCuX]_4$; n = 1 or 2 and X = Cl or Br, complexes with either O_2/CS_2 or O_2 in presence of CS_2: Stoichiometries of the reactions are established spectrophotometrically by molar ratio method[28], Figures-1 and 2, and indicated in equation (3).

$$[(Pip)_nCuX]_4 \xrightarrow[\text{or } 2CS_2/O_2]{O_2/2CS_2} [(Pip)_nCuX]_4\,(CS_2O)_2 \qquad (3)$$

This reaction is considered as Lewis acid-base reaction, in which CS_2 and μ-oxo in $[(Pip)_nCuX]_4O_2$ react as Lewis acid and Lewis base respectively.

Cryoscopic and analytical data for the reaction products of equation (3) are listed in Table-1.

FT-IR measurements: The FT-IR spectral data with their tentative assignments of free piperidine and $[(Pip)_nCuX]_4(CS_2O)_2$, n = 1 or 2, X = Cl or Br as KBr disks are recorded and representative spectra are shown in Figure-3. The spectrum of free piperidine displays two bands at 3445 and 3281 cm^{-1} due to ν_{NH}. These two bands are red shifted in $[(Pip)_nCuX]_4(CS_2O)_2$ to 3438 and 3088cm^{-1} for n = 1 and to 3436 and 3045cm^{-1} for n=2. The spectrum of free piperidine also exhibits δ_{NH} bands at 1652 and 1542cm^{-1} which are disappeared in $[(Pip)_nCuX]_4(CS_2O)_2$ and instead only a strong band at 1632cm^{-1} for n=1 and 1610cm^{-1} for n=2. Such behavior is similar to that reported for $[(Pip)_nCuX]_4O_2$ and $[(Pip)_nCuX]_4(CO_3)_2$[21] and further confirming the bonding of piperidine to the copper center[15]. The splitting of ν_{NH} and δ_{NH} bands could be attributed to the formation of hydrogen bonding between free piperidyl hydrogen and any basic centre in $[(Pip)_nCuX]_4(CS_2O)_2$. By close looking to the range 950-1550cm^{-1} in Figure-3, the spectrum of the ligand is very rich with bands and those bands are shown up in $[(Pip)_nCuX]_4O_2$, n = 1 or 2[15].

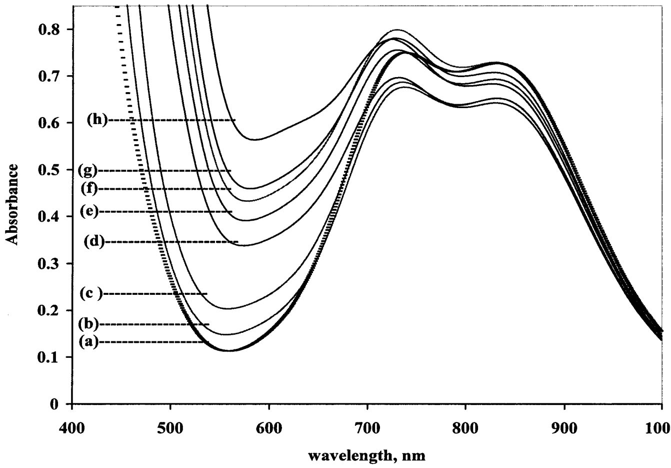


Figure-1: Electronic spectra for the reaction between 1.0x10^{-3} M of $[(Pip)CuCl]_4O_2$ and various concentrations of CS_2 in the range (0.25-9)x10^{-3}M at room temperature in CH_2Cl_2, ($[CS_2]/[(Pip)CuCl]_4O_2]$) = 0 (a), 0.25 (b), 0.5(c), 1(d), 1.5(e), 2(f), 4(g), and 9(h).

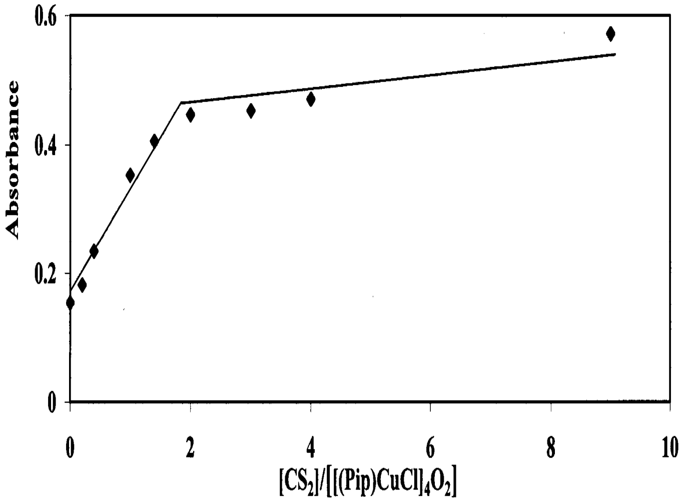


Figure-2: Mole-ratio for the reaction between 1.0x10^{-3}M of $[(Pip)CuCl]_4O_2$ and various concentrations of CS_2 in the range (0.25-9)x10^{-3}M at room temperature in CH_2Cl_2 at a wavelength 600 nm.

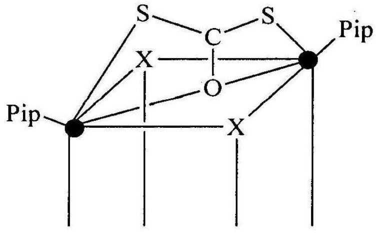
Table-1: Analytical and cryoscopic molecular weight measurements for $[(Pip)_nCuX]_4(CS_2O)_2$; n = 1 or 2 and X = Cl or Br.

Complex	Anal.[a] %						$M^{a,b}$
	C	H	N	Cu	X	S	
$[(Pip)CuCl]_4(CS_2O)_2$	28.1 (28.7)	4.8 (4.8)	6.0 (6.1)	27.7 (27.6)	16.1 (15.4)	14.0 (13.9)	978±20 (920)
$[(Pip)CuBr]_4(CS_2O)_2$	24.0 (24.1)	4.0 (4.0)	5.0 (5.1)	23.2 (23.2)	29.0 (29.1)	12.0 (11.6)	1041±20 (1097)
$[(Pip)_2CuCl]_4(CS_2O)_2$	38.9 (40.0)	6.3 (7.0)	9.0 (8.9)	20.3 (20.2)	11.7 (11.3)	10.0 (10.2)	1240±20 (1260)
$[(Pip)_2CuBr]_4(CS_2O)_2$	35.1 (35.1)	6.1 (6.1)	7.8 (7.8)	17.3 (17.7)	22.9 (22.3)	8.7 (8.9)	1420±20 (1438)

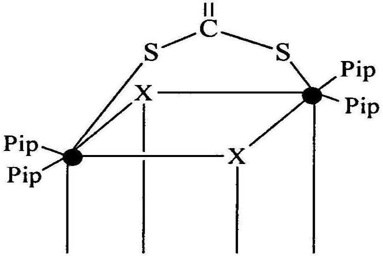
[a]Calculated value in parentheses. [b]Measured value in nitrobenzene at (3-5) x 10^{-2} molal level[17].

The reaction of CS_2 with $[(Pip)_nCuX]_4O_2$ to form $[(Pip)_nCuX]_4(CS_2O)_2$ changes the feature of IR in the range of 950-1550cm^{-1} to a very strong band centred at 1091cm^{-1} and a split medium bands centred at 1415 and 1451cm^{-1} for n =1, rather than a strong sharp band at 1445cm^{-1} in either free piperidine or $[(Pip)_nCuX]_4O_2$[15]. For n = 2, these observations are changed to a very strong band at 1123cm^{-1} followed by a sharp one at 1240cm^{-1} and two intense resolved bands centred at 1440 and 1504cm^{-1}. These new bands are consistent with that reported for xanthate (o-alkyl dithiocarbonate) which showed a similar strong broad band at about 1000-1200cm^{-1} and consequently are taken as evidence for the presence of the dithiocarbonato group in both complexes[27,28].

The different FTIR features between $[(Pip)CuX]_4(CS_2O)_2$ and $[(Pip)_2CuX]_4(CS_2O)_2$ could be referred to a change in the coordination mode of the dithiocarbonato bridging centre, from tridentate in $[(Pip)CuX]_4(CS_2O)_2$ to bidentate in $[(Pip)_2CuX]_4(CS_2O)_2$ so that the coordination number remains six around each Cu centre (Structure-1).



CS_2O^{2-} (tridentate)



CS_2O^{2-} (bidentate)

Structure-1: $[(Pip)CuX]_4(CS_2O)_2$ and $[(Pip)_2CuX]_4(CS_2O)_2$

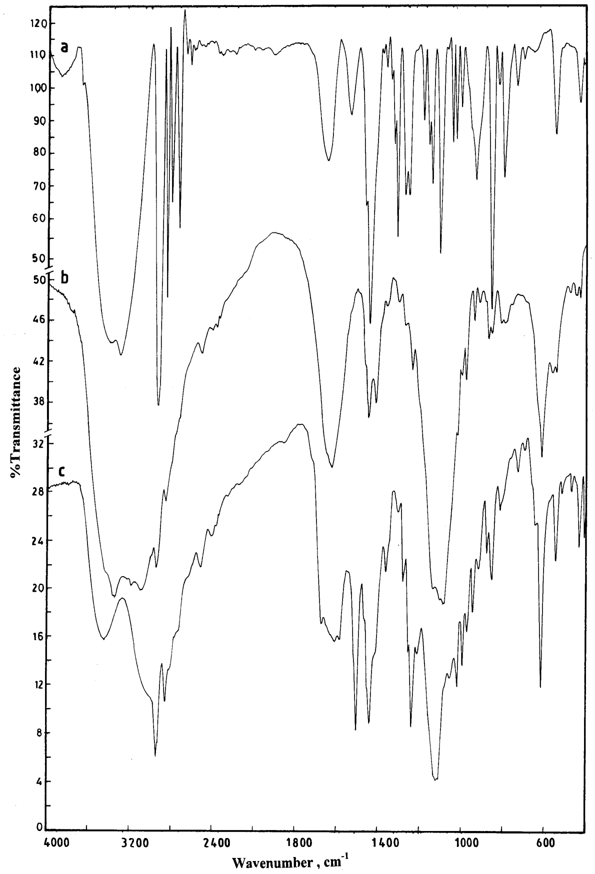


Figure-3: FTIR spectra of: (a) Pip, (b) $[(Pip)CuCl]_4(CS_2O)_2$ and (c) $[(Pip)_2CuCl]_4(CS_2O)_2$.

Electronic spectra: The electronic spectra of $[(Pip)_nCuX]_4(CS_2O)_2$; n = 1 or 2 and X = Cl or Br, Table-1 and shown in Figure-4, exhibit a split maxima in the range 850-720 nm, observed for all investigated complexes. These spectral feautures are consistent with the data reported for $CuCl_3^-$ moiety[15,29,30]. Based on the elemental analyses and FTIR data, it is suggested that each Cu(II) center exists as $CuCl_3^-$ and consequently confirming cubane core structure for $[(Pip)_nCuX]_4(CS_2O)_2$; n = 1 or 2 and X = Cl or Br as given in Structure-1.

The molecular absorptivitiy, ε($M^{-1}cm^{-1}$) values for $[(Pip)_nCuX]_4(CS_2O)_2$; n = 1 or 2 and X = Cl or Br given in Table-2 are found to be i. ε for $[(Pip)_nCuBr]_4(CS_2O)_2 > [(Pip)_nCuCl]_4(CS_2O)_2$ and ii. $[(Pip)CuX]_4(CS_2O)_2 > [(Pip)_2CuX]_4(CS_2O)_2$. These observations are similar to that reported previously for $[(Pip)_nCuX]_4(CO_3)_2$[21].

The values of ε confirmed that these bands are due to charge transfer characteristic of CuX_3^- rather than d-d transitions. Furthermore, the data are similar to that reported for CuX_3^- containing complexes. In addition the spectra of $[(Pip)_nCuX]_4(CS_2O)_2$ display bands at 430-410nm with ε($M^{-1}cm^{-1}$) values of 4000-14000$M^{-1}cm^{-1}$, Table-2, which are absent in the oxo and carbonato analogues[15,21], therefore, it could be referred to CS_2O^{2-}-Cu^{2+} charge transfer transitions. The spectrum of $[(Pip)_2CuX]_4(CS_2O)_2$; X=Cl or Br, exhibits a band for dithiocarbonato group at 605nm and 575nm, with molar absorptivities 810 and 970$M^{-1}cm^{-1}$ for Cl and Br respectively, while $[(Pip)CuX]_4(CS_2O)_2$ show a minimum at that range of wavelength. Such a difference between n = 1 and 2 in $[(Pip)_nCuX]_4(CS_2O)_2$ back up the conclusion which was shown from the infrared spectra that, when n = 1, dithiocarbonato group acts as a tridentate bridging ligand, while for n = 2 it acts as a bidentate ligand (Structure-1).

EPR spectra: The room temperature X-band EPR spectra of the polycrystalline $[(Pip)_nCuX]_4(CS_2O)_2$; n = 1 or 2, X = Cl or Br are shown in Figure-5 and the different spectral parameters are given in Table-2. The spectra of $[(Pip)_nCuX]_4(CS_2O)_2$; X = Cl, n = 1 or 2 and X = Br, n = 1 display uninformative spectra, indicating the presence of exchange coupling since g_1 for all of them, Table-2, lies close to 2.00 implying the d^{z^2} is more populated in the ground state[30]. Based on the elemental analyses, different spectral data and on this observation, a compressed octahedral structure could be assumed for these complexes, Figure-5a-c. $[(Pip)_2CuBr]_4(CS_2O)_2$ displays an axial EPR spectrum, Figure-5d with $g_{\parallel} > g_{\perp} > 2.04$, indicating $d_{x^2-y^2}$ is more populated in the ground state characteristic of an elongated tetragonal distorted octahedral structure[31].

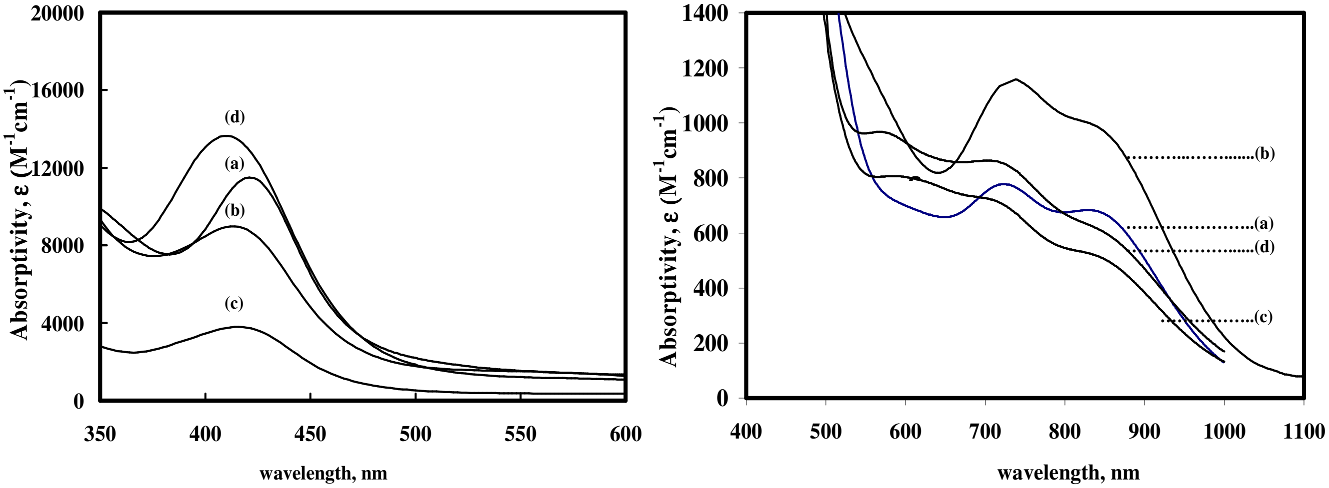


Figure-4: Electronic spectra of $[(Pip)_nCuX]_4(CS_2O)_2$; (a) n=1, X=Cl, (b) n=1, X=Br, (c) n=2, X=Cl, (d) n=2, X=Br, in methylene chloride.

Table-2: Room temperature solid state X-band EPR spectra and electronic spectral data for $[(Pip)_nCuX]_4(CS_2O)_2$; n = 1 or 2, X= Cl or Br, in CH_2Cl_2.

Complex	EPR					Electronic spectra		
	$g_{\parallel}$	$g_{\perp}$	g_1	g_2	g_3	λ_{max} nm ($\varepsilon_{\lambda_{max}}$, $M^{-1}cm^{-1}$)		
$[(Pip)CuCl]_4(CS_2O)_2$	-	-	2.02	2.06	-	840 (680) 720 (780)	610[a]	420(1170)
$[(Pip)CuBr]_4(CS_2O)_2$	-	-	2.01	2.19	-	840 (970) 740(1160)	620[b]	420(9060)
$[(Pip)_2CuCl]_4(CS_2O)_2$	-	-	2.02	2.06	-	840 (520) 720 (710)	605(810)	420(3910)
$[(Pip)_2CuBr]_4(CS_2O)_2$	2.25	2.02	-	-	-	850 (600) 720 (860)	575(970)	410(13750)

[a]broad minimum with shoulder, [b]broad minimum.

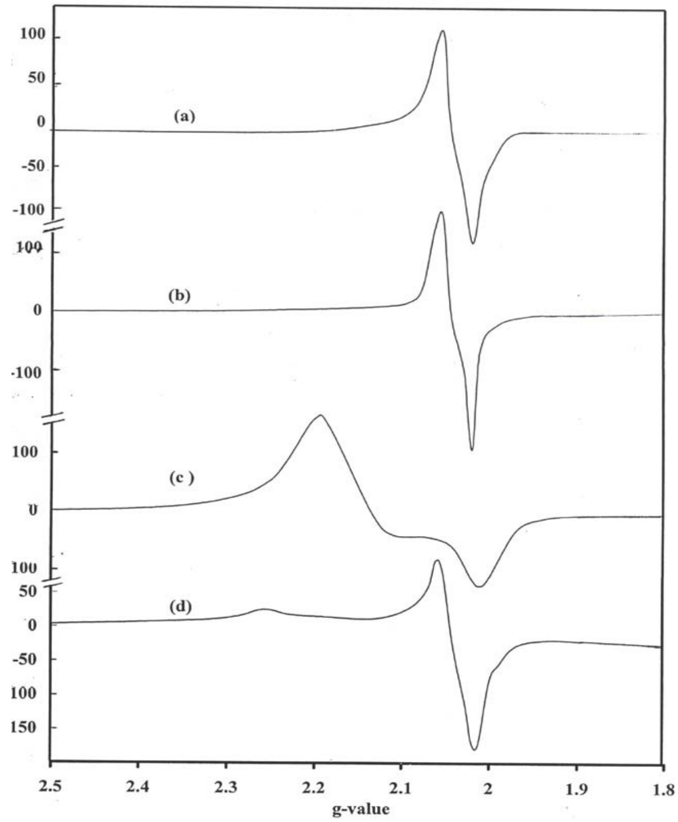
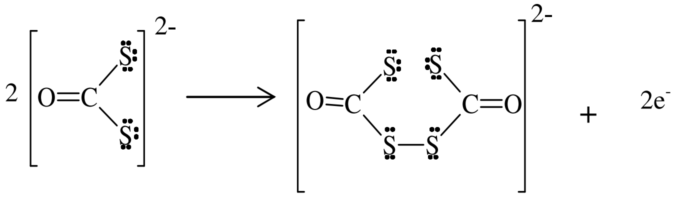


Figure-5: Room temperature solid state X-band EPR spectra for $(Pip)_nCuX]_4(CS_2O)_2$; (a) n = 1, X = Cl , (b) n = 2, X = Cl, (c) n = 1, X = Br, (d) n = 2, X = Br.

Redox activity: The redox activities were studied by cyclic voltammetry (CV) measurements for $[(Pip)_nCuX]_4(CS_2O)_2$; n = 1 or 2, X = Cl or Br, in CH_2Cl_2 solution, made of 0.1 M TBAP. The data are given in Table-3 and shown in Figure-6. The range of 0.7V down to – 0.08V, represents the oxidation of CS_2O^{2-}, Equation (4), because there is no another electrochemical activity species in that range under the same conditions for either $[(Pip)_nCuX]_4O_2$ or CS_2[15].

$$2\,CS_2O^{2-} \longrightarrow C_2S_4O_2^{2-} + 2e^- \qquad (4)$$



Dithiocarbonato moiety shows two consecutive quasi-reversible electron transfer steps, E_1^f (0.37–0.22)V and E_2^f (0.06– -0.01)V, which could be attributed to the different morphology for CS_2O^{2-}. One directly adsorbs on the electrode surface and the other one is opposite to it far from the electrode surface. Cu(II) centres in $[(Pip)_nCuX]_4(CS_2O)_2$ show their electrochemical reduction in the range ((-0.81)–(-1.12)) V. For $[(Pip)CuX]_4(CS_2O)_2$, X = Cl or Br, Cu(II) centers are reduced in a quasi-reversible fashion with E^f = - 0.89 V and - 1.01 V for Cl and Br, respectively. But for $[(Pip)_2CuX]_4(CS_2O)_2$, X = Cl and Br, Cu(II) centers are reduced irreversibly at - 1.12 V and (-0.83 and – 1.03) V, respectively.

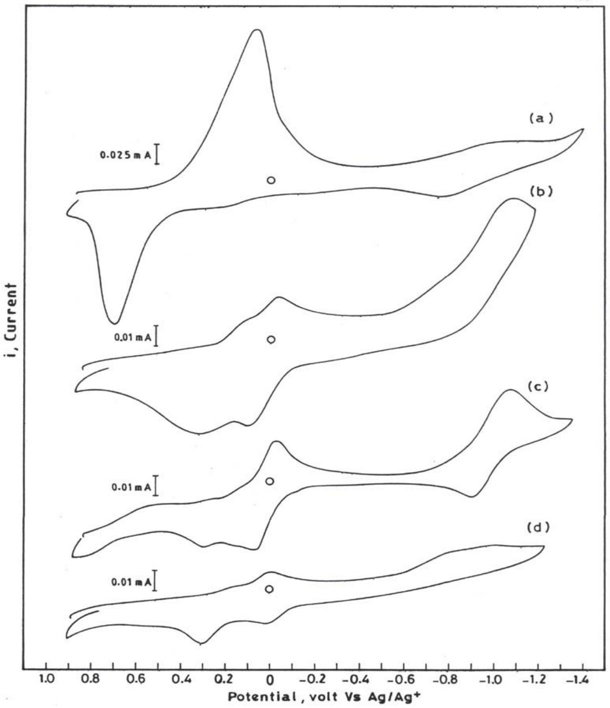


Figure-6: Cyclic voltammetry of $1.0x10^{-3}$M of $[(Pip)_nCuX]_4(CS_2O)_2$; (a) n = 1, X = Cl , (b) n = 2, X = Cl, (c) n = 1, X = Br, (d) n = 2, X = Br in 0.1M TBAP in CH_2Cl_2 solvent using a Pt working electrode at room temperature and scan rate 100 mV/sec.

Catalytic activity: The catalytic activity of all the $[(Pip)_nCuX]_4(CS_2O)_2$ complexes are found to be catalytically inactive for phenol oxidation. The reason could be referred to the dithiocarbonato ligand either by stabilizing Cu(II) centres or its lack of basicity to initiate the catalytical cycle for phenol oxidation.

Conclusion

CS_2 reacts with $[(Pip)_nCuX]_4O_2$; n = 1 or 2 and X = Cl or Br (2:1) to form a new family of $[(Pip)_nCuX]_4(CS_2O)_2$, which represents the first example of dithiocarbonato bridging ligand. From infrared differences for n = 1 and n = 2, regardless X = Cl or Br as well as charge transfer band between dithiocarbonato and Cu(II) at (605-575)nm which exist only for n = 2, one can conclude that dithiocarbonato bridging ligand acts as tridentate for n = 1 and bidentate for n = 2 (Structure-1). Although, $[(Pip)_nCuX]_4(CS_2O)_2$ are catalytically inactive, however, they are electrochemically active and show quasi-reversible peaks for dithiocarbonato ligand in a more positive potentials, when it is compared with Cu(II) centres.

Table-3: Cathodic, anodic and formal electrode potential in volt[a] from cyclic voltammograms for 1.0×10^{-3} M$[(Pip)_nCuX]_4(CS_2O)_2$; n = 1 or 2, X = Cl or Br, at scan rate 100mV/sec and at room temperature in 0.1M TBAP in CH_2Cl_2.

Complex	$(CS_2O)^{2-}$ - domain						Cu (II) - domain		
	E_c^1	E_a^1	E_c^2	E_a^2	E_1^f	E_2^f	E_c	E_a	E_{Cu}^f
$[(Pip)CuCl]_4(CS_2O)_2$	0.05	0.70	- 0.08	0.20	0.37	0.06	- 0.97	- 0.81	- 0.89
$[(Pip)_2CuCl]_4(CS_2O)_2$	0.13	0.32	- 0.04	0.10	0.23	0.06	- 1.12	—	—
$[(Pip)CuBr]_4(CS_2O)_2$	0.13	0.30	- 0.03	0.07	0.22	0.02	- 1.1	- 0.93	- 1.01
$[(Pip)_2CuBr]_4(CS_2O)_2$	0.17	0.30	- 0.02	0.00	0.23	- 0.01	- 0.83 - 1.03	—	—

[a]All potentials were measured with respect to Ag/Ag^+ as a non-aqueous reference electrode. For ferrocene/ferrocenium ion couple versus Ag/Ag^+ reference electrode E_c = - 0.25V, E_a = - 0.05V and E^f = - 0.15V at a scan rate 100mV/sec. 0.4V is formal electrode potential of a reversible one-electron standard ferrocene/ferrocenium ion couple (Fc/Fc^+) versus normal hydrogen electrode (NHE)[15,22].

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