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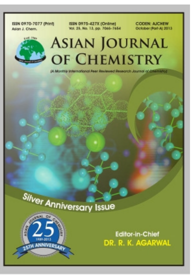

Synthesis and Properties of Tetranuclear Octahalo Copper(II) Complexes, $Pip_4Cu_4X_8$ (Pip = Piperidine, X = Cl or Br) and the Dimer $Pip_4Cu_2Cl_4$ in Aprotic Media

AHMED HASSAN ABDEL-SALAM[1,2] and HISHAM A. ABO-EL-DAHAB[2,3,*]

[1]Department of Chemistry, Faculty of Science, King Abdul-Aziz Univeristy, Jeddah, North Jeddah, Saudi Arabia
[2]Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426, El-Ibrahimeia, Alexandria 21321, Egypt
[3]Department of Chemistry, College of Science, Umm-Al-Qura University, Makkah, Saudi Arabia

*Corresponding author: E-mail: hdahab-41@hotmail.com

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This paper reports a new family of tetranuclear Cu complexes $Pip_4Cu_4X_8$; Pip = piperidine, X = Cl or Br. Two electron oxidant Br_2 has been used to prepare $Pip_4Cu_4Br_8$ from the respective $[PipCuBr]_4$ complex. The dimeric complex, $Pip_4Cu_2Cl_4$, is also prepared by the direct reaction of anhydrous $CuCl_2$ with piperidine in O_2-free CH_2Cl_2. These complexes are isolated as stable solids. They are easily soluble in aprotic solvents as CH_2Cl_2 or $PhNO_2$. Cryoscopic measurements support tetranuclear core structure for $Pip_4Cu_4X_8$.

Key Words: Octahalo copper(II) complexes and dimer, $Pip_4Cu_2Cl_4$.

INTRODUCTION

Progress in understanding the stoichiometry, structural, chemical and photophysical properties of polynuclear halo (amine) Cu(I) complexes has advanced considerably over the previous years[1-7]. Copper(I) halides react quantitatively with piperidine (Pip) in O_2 free CH_2Cl_2 or $PhNO_2$ to form tetranuclear Cu(I) complexes $[(Pip)_nCuX_4]$; n = 1 or 2, X = Cl, Br or I. These complexes are soluble in CH_2Cl_2 and $PhNO_2$. Analytical and cryoscopic data (Table-1) establish the formation of discrete tetranuclear products. The full three-dimensional molecular geometry of $[PipCuI]_4$ was determined using X-ray crystallographic study by El-Sayed *et al.*[8] and Schramm[9].

EXPERIMENTAL

The piperidine (azacyclohexane) (Pip), (Aldrich) was distilled under reduced pressure before use. High purity N_2 was deoxygenated by passage through a column of Alfa-DE-OX solid catalyst and dried by passage through a 60 cm column of dehydrated silica gel and 30 cm column of "$CaCl_2$ and molecular sieves". Bromine (Aldrich) was used as received. Copper(I) halides were prepared as described in literature[10]. Anhydrous $CuCl_2$ was obtained from the hydrate (Alfa) by heating overnight at 120 ºC *in vacuo*. Nitrobenzene was distilled under reduced pressure from P_4O_{10} and stored over 4 Å molecular sieves. Dichloromethane was washed with concentrated H_2SO_4, dried over Na_2CO_3, refluxed over P_4O_{10}, then distilled and stored over anhydrous Na_2CO_3[11].

Synthesis of $Pip_4Cu_4Cl_8$: $Pip_4Cu_4Cl_8$ was prepared by treating a large excess of anhydrous $CuCl_2$ (30 mmol) with piperidine (10 mmol) in CH_2Cl_2 (60 cm^3) similar to the preparation of $N_4Cu_4Cl_8$; N = N,N-diethylnicotinamide[1].

Synthesis of $Pip_4Cu_4Br_8$: A solution of piperidine (2.5 mmol) in anhydrous CH_2Cl_2 (25 cm^3) was flushed with N_2 for 15 min. The appropriate CuBr (2.5 mmol) was added and the mixture was then stirred with bubbling N_2 for 15-20 min. A clear solution of $[PipCuBr]_4$ was obtained. A deoxygenated CH_2Cl_2 solution of Br_2 (1.25 mmol) was then added with

TABLE-1
ANALYTICAL AND CRYOSCOPIC DATA FOR $Pip_4Cu_4X_8$; X = Cl OR Br AND $Pip_4Cu_2Cl_4$ DIMER

Complex	Found (calcd.) %					Molar mass[a]
	C	H	N	X	Cu	
$Pip_4Cu_4Cl_8$	27.8 (27.3)	5.4 (5.0)	6.5 (6.4)	33.0 (32.3)	30.4 (28.9)	848 ± 20 (878)
$Pip_4Cu_4Br_8$	20.9 (22.1)	3.9 (3.6)	4.8 (4.5)	52.9 (51.8)	21.6 (20.6)	1190 ± 20 (1234)
$Pip_4Cu_2Cl_4$	35.5 (39.4)	7.1 (7.2)	8.3 (9.2)	22.0 (23.3)	21.1 (20.9)	590 ±20 (609)

[a]Measured in nitrobenzene at (3-5) × 10^{-2} molal level[12].

stirring to $[PipCuBr]_4$. An immediate colour change to dark brown was observed as a result of Cu(I) oxidation. After filtration the brown product $Pip_4Cu_4Br_8$ was isolated as solid by solvent evaporation.

Synthesis of dimer, $Pip_4Cu_2Cl_4$: A solution of piperidine (2.5 mmol) in anhydrous CH_2Cl_2 (25 cm^3) was added to the appropriate anhydrous $CuCl_2$ (1.25 mmol) and stirred for 15-20 min. An immediate brown complex was observed due to formation of dimer, $Pip_4Cu_2Cl_4$. After filtration the brown product $Pip_4Cu_2Cl_4$ was isolated as solid by solvent evaporation.

All the above complexes were identified by cryoscopic molecular mass determination in $PhNO_2$, (m.p. = 5.7 °C, freezing point depression constant, K_f = 7.0 °C/molal)[12], using Eutechnics precision temperature model 4600 thermometer.

The elemental Cu and halogen (Cl and Br) contents were determined as reported in the literature[13]. All other elemental analyses were determined using LECO CHNS-932 elemental analyzer at Microanalytical laboratory, Chemistry Department, Kuwait University, Kuwait. Molecular mass and analytical data for the isolated complexes are collected in Table-1.

Physical measurements: Electronic spectra for the prepared complexes in CH_2Cl_2 or $PhNO_2$ were measured by Varian Cary-5 double beam spectrometer at room temperature. FT-IR spectra of KBr disks for solid products or KBr plates for liquid ligand were obtained using Perkin Elmer system 2000 FT-IR spectrophotometer at room temperature, at Kuwait University. The 906.5 or 3026.3 cm^{-1} absorption of polystyrene were used for calibration. The EPR spectra for samples of piperidine complexes were measured at the Kuwait University on a Radiopan Varian spectrometer at 100.0000 KHz and at different G modulation amplitude with a rectangular TE 102 cavity and 100 KHz modulation field. Resonance conditions were found at *ca.* 9.7 GHz (X-band) at room temperature only. The field was calibrated with a powder of diphenylpicrylhydrazyl (DPPH; g = 2.0037)[14]. Thermal analyses of these complexes were carried out using a Shimadzu thermal system 50 consisting of TGA-50 and DTA-50. The rate of heating was 10 °C/min. All the measurements were carried out in a current of N_2 flowing at 50 cm^3/min.

RESULTS AND DISCUSSION

Copper(I) halides react quantitatively with piperidine (Pip) in O_2 free CH_2Cl_2 or $PhNO_2$ to form tetranuclear Cu(I) complexes $[(Pip)_nCuX_4]$; n = 1 or 2, X = Cl, Br or I , eqn. 1. Stoichiometry of either $[(Pip)_nCuX]_4$ or their oxo analogues $[(Pip)_nCuX]_4O_2$; n = 1 or 2 and X = Cl, Br or I[8].

$$4Pip + 4CuX \longrightarrow [PipCuX]_4 \tag{1}$$

The tetranuclear octachloro complex, $Pip_4Cu_4Cl_8$ was prepared by the stoichiometric reaction of Pip with excess anhydrous $CuCl_2$ in aprotic solvent, eqn. 2.

$$4Pip + 4CuCl_2 \longrightarrow Pip_4Cu_4Cl_8 \tag{2}$$

Although the corresponding octabromo-complex can not be obtained from $CuBr_2$, it can be synthesized by stoichiometric oxidation of the tetranuclear Cu(I) complex $[PipCuBr]_4$ with Br_2, eqn. 3.

$$[PipCuBr]_4 + 2Br_2 \longrightarrow Pip_4Cu_4Br_8 \tag{3}$$

Many attempts to crystallize $Pip_4Cu_4X_8$ (X = Cl or Br) either from saturated solutions or by diffusing anhydrous either into saturated solutions in CH_2Cl_2 in a closed system were unsuccessful. All the brown products of eqns. 2 and 3 are highly soluble in CH_2Cl_2 and $PhNO_2$. Cryoscopic and analytical data in Table-1 indicate that $Pip_4Cu_4X_8$ (X = Cl or Br) are discrete tetranuclear species. The dimeric complex, $Pip_4Cu_2Cl_4$, was prepared by the stoichiometric reaction of piperidine with anhydrous $CuCl_2$ in aprotic solvent, eqn. 4.

$$4Pip + 2CuCl_2 \longrightarrow Pip_4Cu_2Cl_4 \tag{4}$$

Infrared spectra: The major features of IR spectra of free Pip[15] and $Pip_4Cu_4Cl_8$, $Pip_4Cu_4Br_8$ and $Pip_4Cu_2Cl_4$ complexes as KBr disks (Fig. 1).

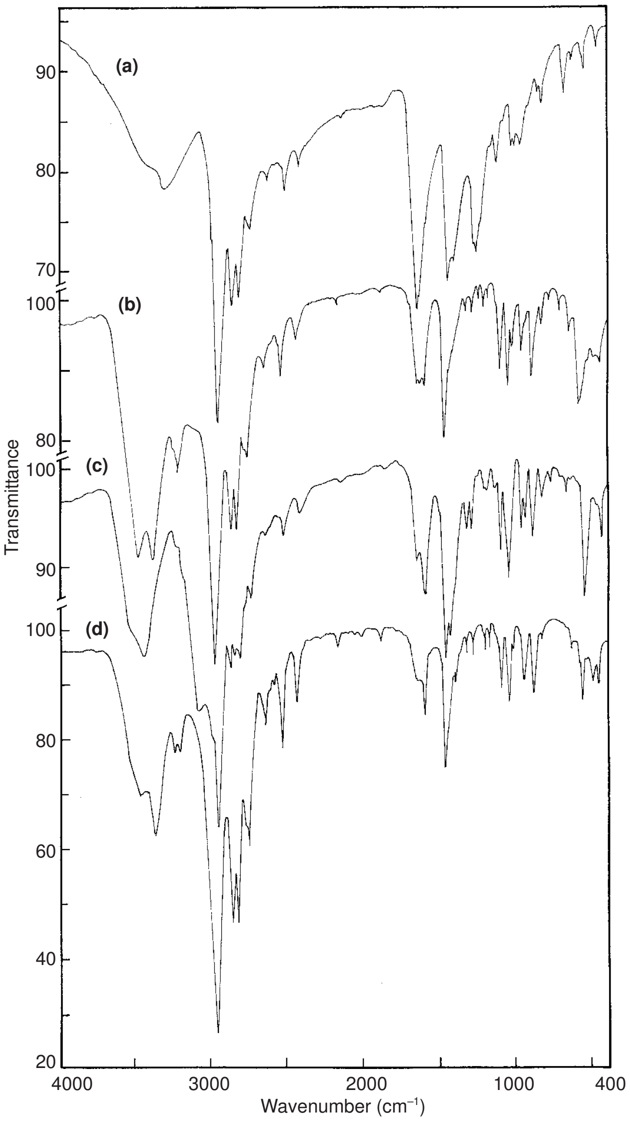


Fig. 1. KBr disk IR spectra (4000-400 cm^{-1}) for (a) piperidine, (b) $Pip_4Cu_4Cl_8$ (c) $Pip_4Cu_4Br_8$ (d) $Pip_4Cu_2Cl_4$

For ν_{NH}, the relative intensity of the band of the free piperidine ligand shown as very weak shoulder at 3425 cm^{-1} and a medium broad band at 3298 cm^{-1} are changed to a strongly splitted resolved band at 3450 and 3355 cm^{-1} for $Pip_4Cu_4Cl_8$ complex. For $Pip_4Cu_4Br_8$ this band appears at 3510 and 3426 cm^{-1}. For the dimeric complex, $Pip_4Cu_2Cl_4$, this band appears at 3450 and 3350 cm^{-1}. These changes in band positions at higher wavenumber are due to the complexation of piperidyl N-H, which are very similar to [PipCuX]$_4$O$_2$; X = Cl or Br[8].

For δ_{NH}, the strong band centered at 1632 cm^{-1} in the free piperidine is changed and splitted to 1631-1589 cm^{-1} for the Cu(II) complex of Pip$_4$Cu$_4$Cl$_8$. For Pip$_4$Cu$_4$Br$_8$ complex, this band is shifted to 1634 and 1583 cm^{-1}. For the dimer complex, Pip$_4$Cu$_2$Cl$_4$, this band appears at 1635 and 1588 cm^{-1}. The bending mode of vibration for CH$_2$-N ($\delta_{CH_2\text{-}N}$) is changed from 1430 cm^{-1} in the free piperidine to higher wavenumber at 1450, 1448 and 1458 cm^{-1} for the Pip$_4$Cu$_4$Cl$_8$, Pip$_4$Cu$_4$Br$_8$ and Pip$_4$Cu$_2$Cl$_4$ complexes, respectively.

A new band appears at 570 and 540 cm^{-1} which is due to ν_{CuCl} and ν_{CuBr} in the Pip$_4$Cu$_4$Cl$_8$ and Pip$_4$Cu$_4$Br$_8$ complexes, respectively. For the dimer, Pip$_4$Cu$_2$Cl$_4$, the ν_{CuCl} band appears at 552 cm^{-1}.

From the above observations, it is concluded that when piperidyl nitrogen is coordinated to the Cu centers, the N-H vibrational modes are sensitive to such coordination[8,16].

Electronic spectra: Electronic spectral data for Pip$_4$Cu$_4$X$_8$, X = Cl or Br and Pip$_4$Cu$_2$Cl$_4$ are listed in Table-2 (Fig. 2). For the octahalo complexes, split maxima in the range of 762 and 847 nm are observed in Fig. 2 which indicates copper centers with a minimum of three halo ligands per each copper center[17,18]. When X is changed from Cl to Br, absorptivitiy (ε, M^{-1} cm^{-1}) is strongly increased (Fig. 2a-b). Similar spectra with about the same broad band positions indicate that the electronic spectra of the above complexes are due to charge transfer between a minimum of three halo ligands with each Cu(II) site. Such a conclusion supports a tetranuclear cubane core structure[1,8,19-21] for Pip$_4$Cu$_4$X$_8$, X = Cl or Br (**Scheme-I**).

The electronic spectrum of dimer, Pip$_4$Cu$_2$Cl$_4$, in CH$_2$Cl$_2$ shows a split maximum in the range of 750 and 844 nm (Fig. 2c), which indicate copper centers with a minimum of three halo ligands per each copper center[17,18]. Similar spectra with about the same broad band positions indicate that the electronic spectra of the above complexes are due to charge transfer between a minimum of three halo ligands with each Cu(II) site[8].

EPR spectra: The X-band ESR spectral data of the polycrystalline of Pip$_4$Cu$_4$X$_8$, X = Cl or Br and Pip$_4$Cu$_2$Cl$_4$ are given in Table-2. All EPR spectra are explained according to Hathaway and Billing[22]. The complexes show an axial spectra with $g_{\parallel} > g_{\perp}$, representing a $d_{x^2-y^2}$ ground state for all of them. Based on the electronic spectra,elemental analyses, IR spectral data and these ESR data square pyramidal arrangement[22-26] could be suggested for these complexes.

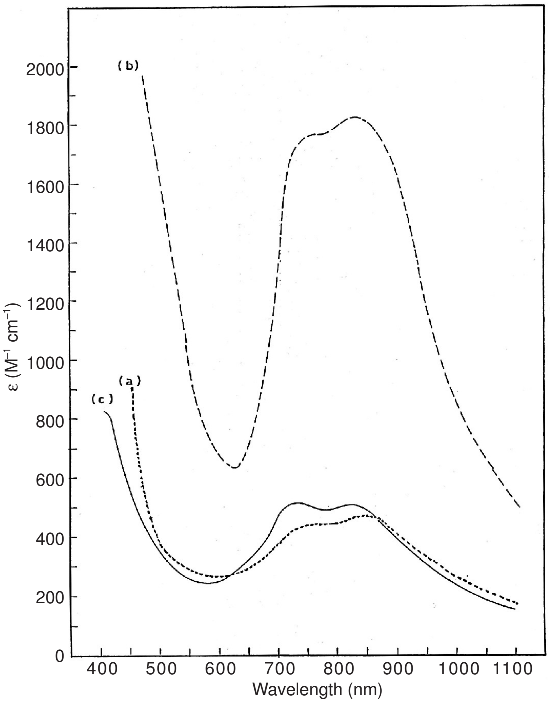
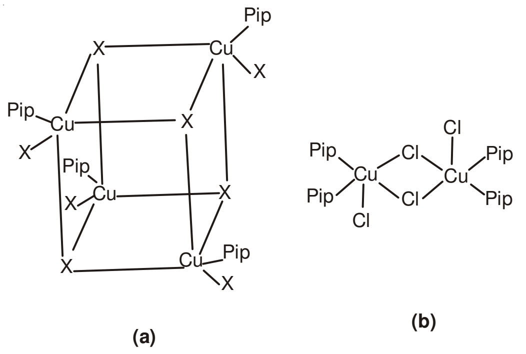


Fig. 2. Electronic spectra of (a) Pip$_4$Cu$_4$Cl$_8$ (b) Pip$_4$Cu$_4$Br$_8$ (c) Pip$_4$Cu$_2$Cl$_4$ in CH$_2$Cl$_2$ at room temperature



(X = Cl orBr)

Scheme-I: Proposed molecular core structure for (a) Pip$_4$Cu$_4$X$_8$ (b) Pip$_4$Cu$_2$Cl$_4$

The room temperature X-band ESR spectra, Fig. 3, displays an axial parameters $g_{\parallel}$ = 2.3 and $g_{\perp}$ = 2.02 characteristics of the population of $d_{x^2-y^2}$ in the ground state for these copper(II) complexes. The average g-value of 2.1 also suggests $d_{x^2-y^2}$ ground state. The appearance of hyperfine lines in the parallel region indicates a copper-ligand bond covalency. However such splitting in the $g_{\perp}$ region is not observed due to the unresolved ligand hyperfine interaction at room temperature. The hyperfine line splitting $A_{\parallel}$ of 142-152 G obtained from the spectra are consistent with a strong distortion from the planarity. In general the empirical factor f = $g_{\parallel}/A_{\parallel}$ is

TABLE-2
ROOM TEMPERATURE SOLID STATE X-BAND EPR AND ELECTRONIC SPECTRAL DATA FOR Pip$_4$Cu$_4$X$_8$, X = Cl OR AND Pip$_4$Cu$_2$Cl$_4$ DIMER AT ROOM TEMPERATURE

Complex	EPR							λ_{max} (nm)^b ($\varepsilon_{\lambda_{max}}$ M^{-1} cm^{-1})	
	$A_{\parallel}^a$	$g_{\parallel}$	$g_{\perp}$	<g>	G	f	α^2		
Pip$_4$Cu$_4$Cl$_8$	–	2.29	2.02	2.11	16.3	–	–	762 (445)	844 (475)
Pip$_4$Cu$_4$Br$_8$	142	2.3	2.01	2.10	38.7	162	0.35	762 (1705)	847 (1685)
Pip$_4$Cu$_2$Cl$_4$	152	2.3	2.02	2.11	16.8	151	0.36	750 (533)	844 (505)

^{a}Units are 10^{-4} cm^{-1}, ^{b}in CH$_2$Cl$_2$ at room temperature.

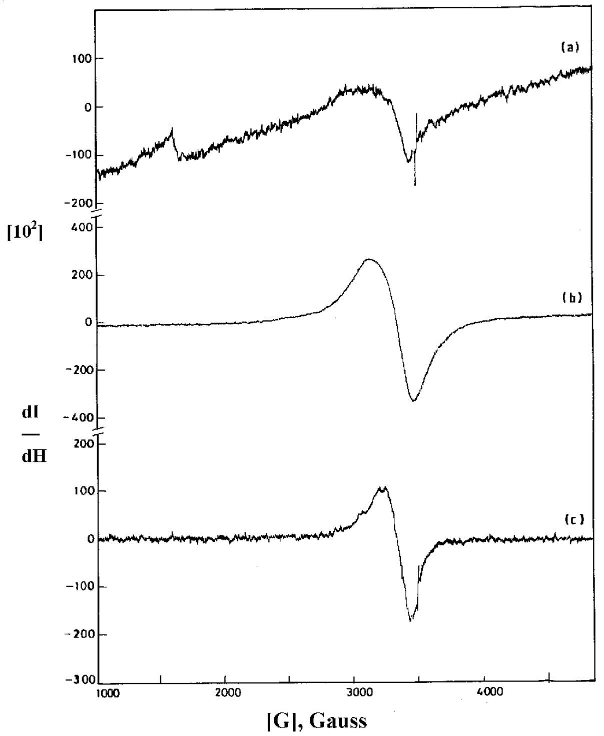


Fig. 3. Room temperature solid state X-band EPR spectra for (a) $Pip_4Cu_4Cl_8$ (b) $Pip_4Cu_4Br_8$ (c) $Pip_4Cu_2Cl_4$

an index of the tetragonal distortion and calculated to be 151-162 cm^{-1}, indicates a strong distortion may be due to the flexible structure. In general the distortion from the planarity towards the tetragonally distorted structure results in decrease in $A_{\parallel}$ and increase in $g_{\parallel}$ as shown in a number of synthetic and biologically active examples involving copper(II). As shown the value of $A_{\parallel}$ is small and in line with that of dominantly strong distorted complex especially tetragonally distorted copper(II) complexes.

The value of the in-planar π bonding parameter α^2 can be estimated from the expression:

$$\alpha^2 = A_{\parallel}/0.036 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

and is found to be 0.36, consistent with mainly covalent copper-in-plane-ligand bonding which in agreement with results obtained for the value of $g < 2.30$.

The spectrum of $Pip_4Cu_4Cl_8$ shows additional signals at 1604 G which gave value of $g = 4.32$ due $\Delta M_s = +2$, characteristic of polynuclear copper(II) complex.

Thermal analysis: The thermogravimetic (TG) and the derivative thermogravimetic (DTG) plots of the complexes in the 50-800 °C range under N_2 are shown in Fig. 4. Their stepwise thermal degradation data are given in Table-3. All complexes show three-stage mass loss.

The thermal analysis data (Table-3), show the following observation: All Cl lost at 293 °C for, $Pip_4Cu_4Cl_8$ while for the dimer, $Pip_4Cu_2Cl_4$ all Cl lost at 541 °C. The thermal degradation data show the molecular structure for all of them, tetranuclear for both $Pip_4Cu_4X_8$, X = Cl or Br and dinuclear for $Pip_4Cu_2Cl_4$.

Conclusion

This paper reports the tetranuclear copper complexes of $Pip_4Cu_4X_8$, X = Cl or Br and $Pip_4Cu_2Cl_4$ dimer. Two electron oxidants Br_2 has been used to prepare $Pip_4Cu_4Br_8$ from the respective $[PipCuBr]_4$ complex. As indicated in **Scheme-I**, both $Pip_4Cu_4Cl_8$ and $Pip_4Cu_4Br_8$ are two molecular units in which the environment around copper centers in each unit are similar, but the ESR spectra indicate a Cu-Cu interaction in $Pip_4Cu_4Cl_8$ which indicate antiferromagnetic interactions.

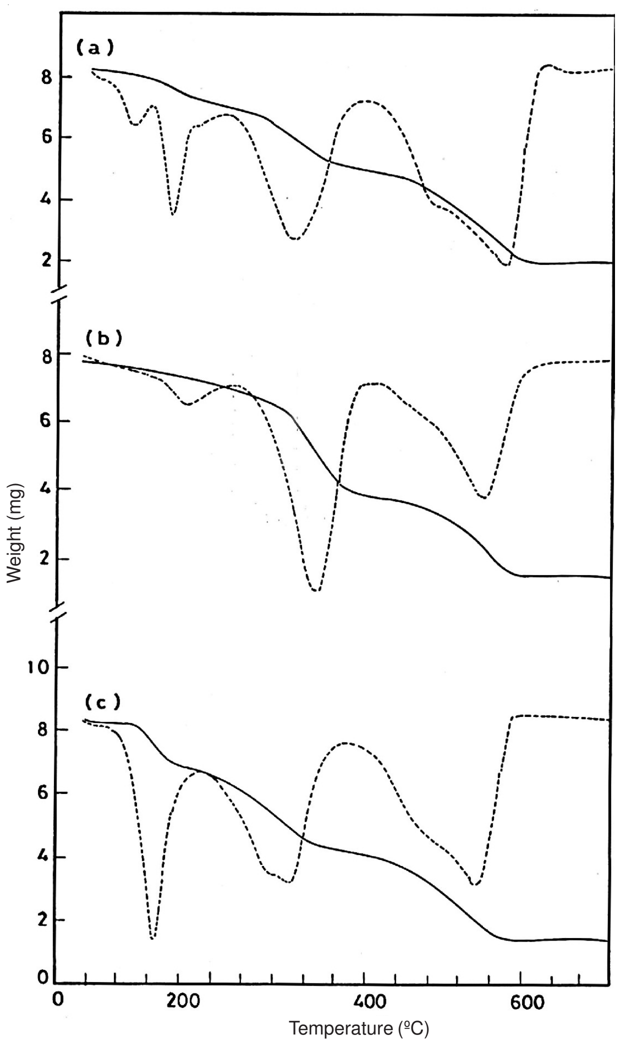


Fig. 4. TG (—) and DTG (----) plots of (a) $Pip_4Cu_4Cl_8$ (b) $Pip_4Cu_4Br_8$ (c) $Pip_4Cu_2Cl_4$

TABLE-3
THERMAL ANALYSIS FOR $Pip_4Cu_4X_8$, X = Cl, Br AND $Pip_4Cu_2Cl_4$

Complex	Molar mass	DTG T_{max} (°C)	Mass loss (%)		Expected ligand lost
			Found	Theoretical	
$Pip_4Cu_4Cl_8$	878	143	8.3	8.1	Cl_2
		293	24.5	24.3	$3Cl_2$
		553	35.9	38.7	4Pip
		–	31.3	28.9	4Cu
$Pip_4Cu_4Br_8$	1234	172	6.8	6.9	Pip
		338	39.5	40.2	3Br + 3 Pip
		556	31.7	32.4	5Br
		–	22.0	20.5	4Cu
$Pip_4Cu_2Cl_4$	–	127	19.0	19.8	Cl + Pip
		300	29.3	28.0	2Pip
		541	32.5	31.4	3Cl + Pip
		–	19.2	20.8	2Cu

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REFERENCES

1. M.A. El-Sayed, *Polyhedron*, **11**, 1261 (1992).
2. K.G. Caulton, G. Davies and E.M. Holton, *Polyhedron*, **9**, 2319 (1990).
3. G. Davies and M.A. El-Sayed, *Inorg. Chem*., **22**, 1257 (1983).
4. G. Davies and M.A. El-Sayed, In eds.: K.D. Karlin and J. Zubieta, In Copper Coordination Chemistry: Biochemical Perspective, Adenine Press, Guilderland, New York, p. 281 (1983) and refs therein.
5. K.D. Karlin and Y. Gultneh, *Prog. Inorg. Chem*., **35**, 219 (1987).
6. (a) M.R. Churchill, G. Davies, M.A. El-Sayed, J.P. Hutchinson and J.A. Zubieta, *Inorg. Chem*., **23**, 783 (1984); (b) M.A. El-Sayed, A. El-Toukhy and G. Davies, *Inorg. Chem*., **24**, 3387 (1985).
7. G. Davies, M.A. El-Sayed, A. El-Toukhy, T.R. Gilbert and K. Nabih, *Inorg. Chem*., **25**, 1929 (1986).
8. M.A. El-Sayed, A.H. Abdel Salam, T.A. El-Zayat, A. El-Dissouky, K.Z. Ismail, *Inorg. Chim. Acta*, **357**, 4057 (2004).
9. V. Schramm, *Inorg. Chem*., **17**, 714 (1978).
10. R.N. Keller and H.D. Wycoff, *Inorg. Synth*., **2**, 1 (1946).
11. M.R. Churchill, G. Davies, M.A. El-Sayed, J.P. Hutchinson and M.W. Rupich, *Inorg. Chem*., **21**, 995 (1982).
12. G. Davies, M.A. El-Sayed and M. Henary, *Inorg. Chem*., **26**, 3266 (1987).
13. (a) G. Schwarzenbach, Complexometric Titration, Methuen Co., London (1957); (b) M. Kalthoff, E.B. Sandell, E.J. Meehan and S. Bruckenstien, Quantitative Chemical Analysis, Macmillan, New York p. 812 (1969).
14. J.E. Wertz and J.R. Botton, Electron Spin Resonance, McGraw-Hill, New York (1972).
15. C.J. Pouchert, The Aldrich Library of Infrared Spectra, edn. 3, Aldrich Chemical Company, Inc., Milwaukee, USA (1989).
16. M.A. El-Sayed, A.H. Abdel Salam, T.A. El-Zayat and A. El-Dissouky, *Transition Met. Chem*., **30**, 616 (2005).
17. G. Davies, A. El-Toukhy, K.D. Onan and M. Veidis, *Inorg. Chim. Acta*, **85**, 98 (1985).
18. M.A. El-Sayed and G. Davies, *Inorg. Chem*., **29**, 213 (1990).
19. G. Davies, M.A. El-Sayed and R. Fasano, *Inorg. Chim. Acta*, **71**, 95 (1983).
20. G. Davies, M.A. El-Sayed, A. El-Toukhy, M. Henary and C.A. Martin, *Inorg. Chem*., **25**, 4479 (1986).
21. M.A. El-Sayed, A. El-Toukhy, K.Z. Ismail, A.A. El-Maradne and G. Davies, *Inorg. Chim. Acta*, **182**, 213 (1991).
22. B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev*., **70**, 143 (1970).
23. B.J. Hathaway, *J. Chem. Soc. Dalton Trans*., 1196 (1972).
24. M.A. El-Sayed and G. Davies, *Inorg. Chem*., **29**, 4891 (1990).
25. B.J. Hathaway, G. Wilkinson, R.D. Gillard and J.A. Mcleverty, Comprehensive Coodination Chemistry, Pergamon, Oxford, Vol. 5, p. 534 (1985).
26. M.R. Churchill, G. Davies, M.A. El-Sayed, M.F. El-Shazly, J.P. Hutchinson and M.W. Rupich, *Inorg. Chem*., **19**, 201 (1980).