Synthesis and Properties of Tetranuclear Octahalo Copper(II) Complexes, $\text{Pip}_4\text{Cu}_4\text{X}_8$ (Pip = Piperidine, X = Cl or Br) and the Dimer $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ in Aprotic Media

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(Received: 3 November 2012;

Accepted: 28 June 2013)

AJC-13718

This paper reports a new family of tetranuclear Cu complexes $\text{Pip}_4\text{Cu}_4\text{X}_8$; Pip = piperidine, X = Cl or Br. Two electron oxidant Br_2 has been used to prepare $\text{Pip}_4\text{Cu}_4\text{Br}_8$ from the respective $[\text{PipCuBr}]_4$ complex. The dimeric complex, $\text{Pip}_4\text{Cu}_2\text{Cl}_4$, 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 $\text{Pip}_4\text{Cu}_4\text{X}_8$.

Key Words: Octahalo copper(II) complexes and dimer, $\text{Pip}_4\text{Cu}_2\text{Cl}_4$.

INTRODUCTION

Progress in understanding the stoichiometry, structural, chemical and photophysical properties of polynuclear halo (amine) Cu(I) complexes has advanced considerably over the previous years¹⁻⁷. Copper(I) halides react quantitatively with piperidine (Pip) in O_2 free CH_2Cl_2 or PhNO_2 to form tetranuclear Cu(I) complexes $[(\text{Pip})_n\text{Cu}_4\text{X}_4]$; $n = 1$ 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 $[\text{PipCuI}]_4$ was determined using X-ray crystallographic study by El-Sayed *et al.*⁸ and Schramm⁹.

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 "CaCl₂ and molecular sieves". Bromine (Aldrich) was used as received. Copper(I) halides were prepared as described in literature¹⁰. Anhydrous CuCl_2 was obtained from the hydrate (Alfa) by heating overnight at 120 °C *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 $\text{Pip}_4\text{Cu}_4\text{Cl}_8$: $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ was prepared by treating a large excess of anhydrous CuCl_2 (30 mmol) with piperidine (10 mmol) in CH_2Cl_2 (60 cm³) similar to the preparation of $\text{N}_4\text{Cu}_4\text{Cl}_8$; N = N,N-diethylnicotinamide¹.

Synthesis of $\text{Pip}_4\text{Cu}_4\text{Br}_8$: A solution of piperidine (2.5 mmol) in anhydrous CH_2Cl_2 (25 cm³) 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 $[\text{PipCuBr}]_4$ 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 $\text{Pip}_4\text{Cu}_4\text{X}_8$; X = Cl OR Br AND $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ DIMER

Complex	Found (calcd.) %					Molar mass ^a
	C	H	N	X	Cu	
$\text{Pip}_4\text{Cu}_4\text{Cl}_8$	27.8 (27.3)	5.4 (5.0)	6.5 (6.4)	33.0 (32.3)	30.4 (28.9)	848 ± 20 (878)
$\text{Pip}_4\text{Cu}_4\text{Br}_8$	20.9 (22.1)	3.9 (3.6)	4.8 (4.5)	52.9 (51.8)	21.6 (20.6)	1190 ± 20 (1234)
$\text{Pip}_4\text{Cu}_2\text{Cl}_4$	35.5 (39.4)	7.1 (7.2)	8.3 (9.2)	22.0 (23.3)	21.1 (20.9)	590 ± 20 (609)

^aMeasured in nitrobenzene at $(3-5) \times 10^{-2}$ molal level¹².

stirring to $[\text{PipCuBr}]_4$. An immediate colour change to dark brown was observed as a result of Cu(I) oxidation. After filtration the brown product $\text{Pip}_4\text{Cu}_4\text{Br}_8$ was isolated as solid by solvent evaporation.

Synthesis of dimer, $\text{Pip}_4\text{Cu}_2\text{Cl}_4$: 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, $\text{Pip}_4\text{Cu}_2\text{Cl}_4$. After filtration the brown product $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ 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, $K_f = 7.0^\circ\text{C/molal}$)¹², using Eutechnics precision temperature model 4600 thermometer.

The elemental Cu and halogen (Cl and Br) contents were determined as reported in the literature¹³. 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 $50\text{ cm}^3/\text{min}$.

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 $[(\text{Pip})_n\text{CuX}_4]$; $n = 1$ or 2 , $\text{X} = \text{Cl}$, Br or I , eqn. 1. Stoichiometry of either $[(\text{Pip})_n\text{CuX}]_4$ or their oxo analogues $[(\text{Pip})_n\text{CuX}]_4\text{O}_2$; $n = 1$ or 2 and $\text{X} = \text{Cl}$, Br or I ⁸.

The tetranuclear octachloro complex, $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ was prepared by the stoichiometric reaction of Pip with excess anhydrous CuCl_2 in aprotic solvent, eqn. 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 $[\text{PipCuBr}]_4$ with Br_2 , eqn. 3.

Many attempts to crystallize $\text{Pip}_4\text{Cu}_4\text{X}_8$ ($\text{X} = \text{Cl}$ 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 $\text{Pip}_4\text{Cu}_4\text{X}_8$ ($\text{X} = \text{Cl}$ or Br) are discrete tetranuclear species. The dimeric complex, $\text{Pip}_4\text{Cu}_2\text{Cl}_4$, was prepared by the stoichiometric reaction of piperidine with anhydrous CuCl_2 in aprotic solvent, eqn. 4.

Infrared spectra: The major features of IR spectra of free Pip¹⁵ and $\text{Pip}_4\text{Cu}_4\text{Cl}_8$, $\text{Pip}_4\text{Cu}_4\text{Br}_8$ and $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ complexes as KBr disks (Fig. 1).

Fig. 1. KBr disk IR spectra ($4000\text{--}400\text{ cm}^{-1}$) for (a) piperidine, (b) $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ (c) $\text{Pip}_4\text{Cu}_4\text{Br}_8$ (d) $\text{Pip}_4\text{Cu}_2\text{Cl}_4$

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 $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ complex. For $\text{Pip}_4\text{Cu}_4\text{Br}_8$ this band appears at 3510 and 3426 cm^{-1} . For the dimeric complex, $\text{Pip}_4\text{Cu}_2\text{Cl}_4$, 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 $[\text{Pip}_4\text{CuX}]_4\text{O}_2$; X = Cl or Br⁸.

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

A new band appears at 570 and 540 cm^{-1} which is due to ν_{CuCl} and ν_{CuBr} in the $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ and $\text{Pip}_4\text{Cu}_4\text{Br}_8$ complexes, respectively. For the dimer, $\text{Pip}_4\text{Cu}_2\text{Cl}_4$, 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 $\text{Pip}_4\text{Cu}_4\text{X}_8$, X = Cl or Br and $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ 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, absorptivity (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 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 $\text{Pip}_4\text{Cu}_4\text{X}_8$, X = Cl or Br (**Scheme-I**).

The electronic spectrum of dimer, $\text{Pip}_4\text{Cu}_2\text{Cl}_4$, in CH_2Cl_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) site⁸.

EPR spectra: The X-band ESR spectral data of the polycrystalline of $\text{Pip}_4\text{Cu}_4\text{X}_8$, X = Cl or Br and $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ are given in Table-2. All EPR spectra are explained according to Hathaway and Billing²². 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 arrangement²²⁻²⁶ could be suggested for these complexes.

The room temperature X-band ESR spectra, Fig. 3, displays an axial parameters $g_{\parallel} = 2.3$ and $g_{\perp} = 2.02$ characteristics

Fig. 2. Electronic spectra of (a) $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ (b) $\text{Pip}_4\text{Cu}_4\text{Br}_8$ (c) $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ in CH_2Cl_2 at room temperature

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

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 $\text{Pip}_4\text{Cu}_4\text{X}_8$, X = Cl OR AND $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ DIMER AT ROOM TEMPERATURE

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

^aUnits are 10^{-4}cm^{-1} , ^bin CH_2Cl_2 at room temperature.

Fig. 3. Room temperature solid state X-band EPR spectra for (a) $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ (b) $\text{Pip}_4\text{Cu}_4\text{Br}_8$ (c) $\text{Pip}_4\text{Cu}_2\text{Cl}_4$

an index of the tetragonal distortion and calculated to be $151\text{--}162\text{ cm}^{-1}$, 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 $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ 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 thermogravimetric (TG) and the derivative thermogravimetric (DTG) plots of the complexes in the $50\text{--}800\text{ }^{\circ}\text{C}$ 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 $293\text{ }^{\circ}\text{C}$ for, $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ while for the dimer, $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ all Cl lost at $541\text{ }^{\circ}\text{C}$. The thermal degradation data show the molecular structure for all of them, tetranuclear for both $\text{Pip}_4\text{Cu}_4\text{X}_8$, $\text{X} = \text{Cl}$ or Br and dinuclear for $\text{Pip}_4\text{Cu}_2\text{Cl}_4$.

Conclusion

This paper reports the tetranuclear copper complexes of $\text{Pip}_4\text{Cu}_4\text{X}_8$, $\text{X} = \text{Cl}$ or Br and $\text{Pip}_4\text{Cu}_2\text{Cl}_4$ dimer. Two electron

Fig. 4. TG (—) and DTG (---) plots of (a) $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ (b) $\text{Pip}_4\text{Cu}_4\text{Br}_8$ (c) $\text{Pip}_4\text{Cu}_2\text{Cl}_4$

TABLE-3 THERMAL ANALYSIS FOR $\text{Pip}_4\text{Cu}_4\text{X}_8$, $\text{X} = \text{Cl}$, Br AND $\text{Pip}_4\text{Cu}_2\text{Cl}_4$					
Complex	Molar mass	DTG T_{max} ($^{\circ}\text{C}$)	Mass loss (%)		Expected ligand lost
			Found	Theoretical	
$\text{Pip}_4\text{Cu}_4\text{Cl}_8$	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
$\text{Pip}_4\text{Cu}_4\text{Br}_8$	1234	172	6.8	6.9	Pip
		338	39.5	40.2	$3\text{Br} + 3\text{Pip}$
		556	31.7	32.4	5Br
		—	22.0	20.5	4Cu
$\text{Pip}_4\text{Cu}_2\text{Cl}_4$	—	127	19.0	19.8	$\text{Cl} + \text{Pip}$
		300	29.3	28.0	2Pip
		541	32.5	31.4	$3\text{Cl} + \text{Pip}$
		—	19.2	20.8	2Cu

oxidants Br_2 has been used to prepare $\text{Pip}_4\text{Cu}_4\text{Br}_8$ from the respective $[\text{PipCuBr}]_4$ complex. As indicated in **Scheme-I**, both $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ and $\text{Pip}_4\text{Cu}_4\text{Br}_8$ 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 $\text{Pip}_4\text{Cu}_4\text{Cl}_8$ which indicate antiferromagnetic interactions.

ACKNOWLEDGEMENTS

The author thanks Prof. Dr. Mohamed A. El-Sayed, Chemistry Department, Faculty of Science, Alexandria University, for support and for valuable discussions and Prof. Dr. Ali El-Dissouky, Kuwait University for assistance with measurements.

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