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Unexpected behaviour of copper(I) towards a tridentate Schiff base: synthesis, structure and properties of new Cu(I)–Cu(II) and Cu(II) complexes

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Abstract

The reaction of CuBr with 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine L afforded a new Cu(I)–Cu(II) derivative $[CuBrL]_2[Cu_2Br_4]$ (1), while the reaction of $[Cu(CH_3CN)_4]PF_6$ with L in THF yielded the new Cu(I) compound $CuL(THF)(CH_3CN)PF_6$ (2). Derivative 2 further reacted with halogenated solvents to yield halogeno-Cu(II) salts, $[CuClL]PF_6$ (3) using CHCl₃ and $[CuBrL]Br_3$ (4) using CHBr₃. Compounds 1, 3 and 4 have been fully characterised by X-ray crystallography; they contain essentially similar $[CuXL]^+$ cations with a square planar copper(II) co-ordination. However, the structure of compound 1 must be viewed as built of tetranuclear units since two $[Cu^{II}BrL]^+$ cations are bridged by a $[Cu_2^{I}Br_4]^2$ anion with a rather strong $Cu^{II}...Br$ (2.689(2) Å) secondary interaction. These secondary interactions (Cu^{II} cation...FPF₅ or Br anion) are weaker in 3 and 4. The electrochemical properties of compounds 1–4 are discussed, too. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper complexes; Disubstituted pyridine ligand; Crystal structures; Electrochemistry

1. Introduction

The co-ordinating ability of the 2,6-diacetylpyridinebis(imine) ligands (Scheme 1), which may be viewed as terpyridine analogues, i.e. planar NNN terdentate ligands, has been studied for long; numerous wernerian complexes of first row transition metals are well known. To date most of these complexes are either five or six co-ordinate derivatives containing one or two neutral tridentate meridionally co-ordinated ligands [1].

This family of ligands has recently found a renewal of interest since: (i) the unexpected and recent discovery that such complexes, in particular the pyridine-2,6-diimine iron(II) and cobalt(II) complexes, may act as very active catalysts for olefin polymerisation render them more attractive for chemists [2]; (ii) in addition, metal complexes derived from N_3 terdendate ligands have been shown to form a large variety of molecular architectures, ranging from macrocyclic helicates to infinite coordination polymers [3].



Scheme 1.

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In regard to copper chemistry, only few examples have been fully characterised till today, e.g. with copper(II) [CuL'(NO₃)₂] and very recently [CuL''₂](PF₆)₂ [4] (Scheme 1) and with copper(I) a thermotropic liquidcrystalline complex with a L-type ligand, non-mesomorphic itself, although bearing long chains [5].

Considering the great potentiality of such Schiff base type species, we became thus interested in studying their co-ordination especially to copper(I) and to other metals. As we were starting this work, Halcrow published results related to the chemistry of 2,6-bis(iminomethyl)pyridine copper derivatives and described the X-ray structure of a copper(I) complex $[CuL_2''']BF_4$ (Scheme 1) [6].

In this paper, we present some unexpected results related to the reactions of copper(I) derivatives towards the 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine L.

2. Experimental

2.1. General procedures

All reactions were performed in Schlenk tubes under a dry dioxygen-free dinitrogen atmosphere. Solvents were distilled using standard techniques and were thoroughly deoxygenated before use. Elemental analyses were performed by the 'Service Central d'Analyses du CNRS', Vernaison, France. IR spectra were obtained with a Nicolet Nexus spectrometer (KBr pellets). ESR spectra were run on a Bruker Elaxys spectrometer (X-band). NMR spectra were recorded with a Bruker AMX 400 MHz. UV-Vis spectra were recorded on an Anthélie Secoman spectrometer. The solid state magnetic susceptibility measurements were carried out on powder samples using either a Gouy balance Johnson Matthey at room temperature (r.t.) or a commercial SQUID magnetometer from Quantum Design, from 2 to 250 K. The susceptibilities were corrected for the intrinsic diamagnetism of the sample container. The electrochemical measurements were performed, under Ar, using a microAutolab apparatus from Eco-(Roucaire), and a three compartment chemie micro-electrochemical cell equipped with a rotating disk electrode (Metrohm) as a working electrode (Pt disk, $\emptyset = 0.3$ cm). The reference potential was that of the ferrocenium/ferrocene (Fc⁺/Fc) couple. The solvents were commercial acetonitrile and THF; tetrabutylammonium hexafluorophosphate was the supporting electrolyte purified by standard techniques. [Cu(CH₃CN)₄]PF₆ [7] and the ligand L [8] were prepared as described in the literature. CuBr was purchased from Aldrich.

2.2. Preparations

2.2.1. $[CuBr(C_{33}H_{43}N_3)]_2[Cu_2Br_4]$ (1)

A filtered THF solution of CuBr (0.6 g, 4.2 mmol) was transferred in a Schlenk flask containing the ligand L (1.0 g, 2.1 mmol). The mixture was heated under reflux for 3 h. A solution colour change from light yellow to orange occurred immediately. After cooling to r.t., the orange solution was concentrated to dryness under vacuum and then the solid extracted with about 30 mL of CH₂Cl₂. After filtration, the resulting solution was layered with 30 mL of hexane; after 3 days, orange-red monocrystals were obtained (yield 60%). Anal. Found: C, 46.3; H, 5.0; N, 4.7. Calc. for C₆₆H₈₆Br₆Cu₄N₆: C, 46.7; H, 5.1; N, 4.9%. IR (KBr pellets, \bar{v}_{max} cm⁻¹): 2965s, 2927s and 2868m (v_{CH}); 1615m and 1585s (v_{CN imine}); 1466s, 1442m, 1382m, 1367s, 1321m, 1265s, 1216m, 1180vw, 1103w, 1057m, 1037m, 986vw, 938w, 835vw, 816m, 799s, 779m, 760w, 740w, 694vw, 651vw, 572vw. $\mu_{298 \text{ K}} = 2.57 \mu_{\text{B}}$. UV–Vis 312(4.31), $(\lambda_{\rm max}/\rm nm)$ $(CH_3CN)(\log \varepsilon)): 234(4.66),$ 482(3.64).

2.2.2. $Cu(C_{33}H_{43}N_3)(CH_3CN)(THF)PF_6$ (2)

A stoichiometric mixture of $[Cu(CH_3CN)_4]PF_6$ (1.0 g, 2.68 mmol) and L (1.29 g, 2.68 mmol) was transferred in a round Schlenk flask. THF (100 mL) was poured via canulation and the mixture was refluxed for 1.5 h. Immediately the solution colour turned from light yellow to dark brown. After cooling to r.t., the brown solution was filtered off and concentrated to dryness under vacuum. The dark crude product was washed with pentane and then recrystallised in THF and left at -20 °C for 2 days before filtration (crude yield 80%). Anal. Found: C, 57.8; H, 6.2; N, 6.4. Calc. for C39H54CuF6N4OP: C, 58.3; H, 6.8; N, 7.0%. IR (KBr pellets, \bar{v}_{max} cm⁻¹): 2962s, 2927s and 2869m (v_{CH}); 2270vw (v_{CN,CH,CN}), 1710m, 1635m and 1589s (v_{CN} imine); 1464s, 1440s, 1370s, 1327m, 1310m, 1255s, 1242s, 1210m, 1144w, 1102m, 1059m, 1043m, 1017m, 936w, 842s, vb (v_{PF}), 815s, 775m, 756m, 740w, 716w, 602vw, 558s (δ_{PF}), 447vw, 390vw. NMR ¹H(THF- d_8 , δ ppm): 1.16 (d, 24, CH(CH₃)₂), 2.35 (s, 3, CH₃CN), 2.42 (s, 6, N=CCH₃), 2.81 (m, 4, CH(CH₃)₂), 7.18 (m, 4, H_{arvl}), 7.26 (d, 2, H_{arvl}), 8.33 (d, 2, H_{Py}), 8.52 (t, 1, H_{Py}).

2.2.3. $[CuCl(C_{33}H_{43}N_{3})]PF_{6}$ (3)

Compound **2** (0.50 g, 0.68 mmol) was dissolved in chloroform (30 mL) at r.t. The mixture was left under stirring for 1 h. After filtration and concentration under vacuum, the resulting solution was kept at r.t. for 3 days. Compound **3** slowly precipitated as dark-orange microcrystals, which were filtered and dried (yield 85%). *Anal.* Found: C, 53.6; H, 5.8; N, 5.7. Calc. for $C_{33}H_{43}CuF_6N_3P\cdot0.1CHCl_3$: C, 53.9; H, 5.9; N, 5.7%. (KBr pellets, \bar{v}_{max}/cm^{-1}): 2961s, 2929m and 2870m

 (v_{CH}) ; 1621m and 1592s $(v_{CN} \text{ imine})$; 1463m, 1441w, 1383w, 1375m, 1323w, 1266s, 1219w, 1181w, 1104m, 1094m, 1058m, 1042m, 989w, 938m, 830vs-vb, 814s, 800s, 778s, 760m, 741m, 558s, 456vw, 435w, 405m, 370w, 327vw, 266w. $\mu_{298 \text{ K}} = 1.82 \mu_{B.}$

Single crystals of 3 were obtained in the NMR tube used to run the ¹H NMR spectra of 2 in $CDCl_3$.

2.2.4. $[CuBr(C_{33}H_{43}N_3)]Br_3$ (4)

Compound 2 (1.05 g, 1.43 mmol) was dissolved at r.t. with stirring in bromoform (30 mL). After filtration and concentration under vacuum, the resulting solution was kept at r.t. Compound 4 slowly precipitated as orange brown crystals, which were filtered and dried (yield 85%). Although the crystal structure determination showed a formula 4·2CHBr₃, the elemental analysis is consistent with a lower amount of bromoform. *Anal.* Found: C, 33.7; H, 3.5; N, 3.4. Calc. for $C_{33}H_{43}Br_4CuN_3 \cdot 1.5CHBr_3$: C, 33.3; H, 3.6; N, 3.4%. IR (KBr pellets, \bar{v}_{max} cm⁻¹): 2967s, 2925m and 2867m (v_{CH}), 1616m and 1586s (v_{CN} imine), 1463m, 1443m, 1369s, 1321m, 1265s, 1216m, 1150m, 1092m, 1057m, 1040m, 985w, 938w, 839w, 801s, 778m, 760w, 736w, 692w, 654s, 570w, 537w, 450w, 438w, 356w, 314w.

2.3. X-ray structure analyses

Crystals of 1, 3 and 4.2CHBr₃ suitable for X-ray studies were obtained from CH₂Cl₂, CDCl₃ and CHBr₃ solutions, respectively, and were mounted on a Nonius Kappa CCD diffractometer. The unit cell determinations and data collections were carried out with Mo Ka radiation (0.71073 Å) at low temperature (110 K). The measured intensities were reduced with DENZO program [9]. The structures were solved via direct methods (1, 3)or Patterson (4) with SHELXS-97. All models were further refined with full-matrix least-squares methods (SHELXL-97) based on $|F^2|$ [10a]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and refined with a riding model. While the determinations of the crystal structures of 1 and 3 have been carried without particular problems (for 3, the absolute-structure parameter [10b] of 0.003(7) confirms the absolute structure reported here), that of 4 merits some comments. The crystals of 4 were of poor quality (large reflections) and very thin $(0.6 \times 0.5 \times 0.04 \text{ mm})$. Attempts to cut smaller (more regular) samples failed. Moreover, the measured crystal has been accidentally lost before the treatment of data, and consequently, no absorption correction could be applied. The structure of 4.2CHBr₃ has been deduced from Patterson synthesis which allowed to locate the six bromine atoms of two solvent bromoform molecules. Further difference Fourier analyses clearly revealed at first the Br₃⁻ anion and subsequently all atoms of the cation and the carbon atoms of the solvent. Because the molecular geometry found for the cation in 4 closely resembles those observed in 1 and 3 and because the formation of 4 is interesting from a chemical point of view, we decided to introduce this structure in the actual paper, in spite of rather bad final statistics. Crystallographic data and final discrepancy factors are gathered in Table 1.

3. Results and discussion

3.1. Syntheses, spectroscopic and magnetic studies

Reaction of the copper(I) bromide CuBr with 2,6bis[1-(2,6-diisopropyl phenylimino)ethyl]pyridine (L) in THF at reflux afforded a new copper salt 1 for which the elemental analysis is in good agreement with the formula $Cu_4Br_6L_2$. If we consider in this complex the presence of an usual L ligand in its neutral state, the unexpected value for the Cu/Br ratio (4/6) indicates the presence of copper in at least two oxidation states, presumably Cu(I) and Cu(II). The presence of Cu(II) was confirmed by magnetic studies since magnetic susceptibility measurements run in the range 2-250 K reveal 1 to be paramagnetic and that it follows a Curie Law with the Curie constant C of 0.82 emu K mol⁻¹, a value typical of two magnetically diluted copper(II) centres (S = 1/2). The EPR powder spectrum of compound 1 recorded at r.t. displays a signal centred at g = 2.096, besides, the EPR spectrum of a frozen solution of 1 (CH₂Cl₂, 150 K) exhibits the usual patterns of a Cu(II) atom in an elongated axial environment (half filled $d_{x^2} - d_{y^2}$ level) i.e. $g_{1/2} = 2.129, g_{\perp} = 2.063, A_{1/2} = 170$ G. Since the X-ray studies indicate the asymmetric unit consists of [CuBrL] and [Cu₂Br₄] moieties (see below), these data indeed agree with the formula 2[Cu^{II}BrL]⁺ $[Cu_2^I Br_4]^2$ (Scheme 2). Co-ordination of the tridentate ligand to a copper centre was clearly indicated by an important shift of the $v_{C = imine}$ from 1644 to 1585 cm⁻¹ on the infrared spectrum (KBr pellets).

With the aim to better understand the behaviour of copper(I) complexes towards the ligand L, we planned to study the reaction of L with the salt $[Cu(CH_3CN)_4]PF_6$. This reaction, carried out by refluxing stoichiometric amounts of the two compounds in THF, afforded a new derivative for which elemental analysis is in good agreement with the following formula CuL(CH₃CN)(THF)PF₆ (2) (Scheme 2). In addition to the usual tridentate ligand features [9], the ¹H NMR spectrum of 2, recorded in THF- d_8 , exhibits a supplementary resonance at 2.35 ppm indicative of the presence of a co-ordinated acetonitrile molecule. This observation is corroborated by the very weak band pointed out at 2270 cm⁻¹ on the infrared spectrum (KBr pellets). Furthermore, a strong band at 1589

Table 1

Crystal data and structure refinement for compounds $[CuBrL]_2[Cu_2Br_4]$ (1), $[CuClL]PF_6$ (3) and $[CuBrL]Br_3$ (4)

Compound	1	3	4·2CHBr ₃
Empirical formula	C ₃₃ H ₄₃ Br ₃ Cu ₂ N ₃ ^a	C33H43ClCuF6N3P	C ₃₅ H ₄₅ Br ₁₀ CuN ₃
M	848.51	725.66	1370.38
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/a$	<i>P</i> 2 ₁	$P\overline{1}$
Crystal colour, habit	red, prism	red, irregular	green, plate
a (Å)	18.721(1)	8.7956(2)	10.1152(3)
b (Å)	8.854(1)	11.9903(2)	10.4189(2)
c (Å)	21.103(1)	16.8802(4)	21.8128(7)
α (°)			102.808(1)
β (°)	108.143(5)	101.53(2)	92.071(1)
γ (°)			97.678(1)
V (Å ³)	3324.0(4)	1744.30(6)	2216.4(2)
Ζ	4	2	2
$D_{\text{calc}} (\text{mg m}^{-3})$	1.696	1.382	2.053
Absorption coefficient (mm ⁻¹)	4.913	0.807	9.535
<i>F</i> (000)	1700	754	1310
Crystal size (mm ⁻³)	$0.2 \times 0.15 \times 0.1$	$0.45 \times 0.25 \times 0.15$	0.6 imes 0.5 imes 0.04
θ Range (°) for coll.	2.29-26.68	2.88-27.54	2.03–29.15
hkl/ranges	$-23+22, -11+8, -26 \pm 26$	$\pm 11, -15+14, \pm 21$	$-11+13, -9+13, \pm 29$
Reflections collected/unique/gr[$I > 2\sigma(I)$]	$9518/6281/4154 \ [R(int) = 0.0537]$	6659/6659/6535	$11350/10126/8143 \ [R(int) = 0.0611]$
Data/restraints/parameters	6281/0/367	6659/1/406	10126/0/442
Final R indices	$R_1^{b} = 0.0561,$	$R_1 = 0.0256,$	$R_1 = 0.1029,$
$[I > 2\sigma(I)]$	$wR_2^{\ c} = 0.0962$	$wR_2 = 0.0672$	$wR_2 = 0.2685$
R indices (all data)	$R_1^{b} = 0.1092,$	$R_1 = 0.0264,$	$R_1 = 0.1215,$
	$wR_2^{\ c} = 0.1143$	$wR_2 = 0.0681$	$wR_2 = 0.2931$
$W^{\mathrm{d}}(a, b)$	0.0195, 17.6244	0.0308, 0.4815	0.2, 0.0
Goodness-of-fit on F^2	1.053	1.083	1.217
$ \rho_{\rm max}, \ \rho_{\rm min} \ ({\rm e} \ {\rm \AA}^{-3}) $	0.736, -0.674	0.303, -0.410	2.832, -4.076

^a The empirical formula corresponds to the asymmetric unit which is consistent to the half of the chemical formula.

^b $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|.$

 ${}^{c}wR_{2} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}]^{\Sigma}[w(F_{o}^{2})^{2}]^{1/2}.$

^d $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$.





cm⁻¹ attributable to the CN imine bond reveals the co-ordination of the tridentate ligand to the copper centre. Any effort to obtain suitable single crystals for an X-ray analysis was unsuccessful, the structure for this compound remains unresolved so far it might be polynuclear since the FAB mass spectrum, not clearly elucidated, displayed peaks at m/z values higher than those expected for mononuclear species.

It is noteworthy that our attempts to obtain a NMR

spectrum of complex **2** from a CDCl₃ solution failed because it reacted with the solvent affording a paramagnetic derivative [CuClL]PF₆ (**3**) for which single crystals came out from the deuterated solvent (Scheme 2). Basically on its IR spectrum we observed the disappearance of the band at 1710 cm⁻¹ and a slight shift of the band characteristic of the imine function from 1589 to 1592 cm⁻¹. The complex **3** can be also prepared from CHCl₃ solutions of **2**. Similar experiments conducted at r.t. in CHBr₃ afforded a new copper(II) salt 4 which analysed consistently for CuLBr₄·1.5CHBr₃; its X-ray analysis actually revealed the presence of a tribromide anion Br_3^- (see below).

3.2. Crystal structures

Compound 1 crystallises in the monoclinic space group $P2_1/a$ and its crystal structure is consistent with the

presence of two cationic entities $[CuBrL]^+$ related to each other by an inversion centre and one centrosymmetric dimer $[Cu_2Br_4]^{2-}$ (Fig. 1). For compound **3** (monoclinic space group $P2_1$), the asymmetric unit consists of a $[CuClL]^+$ cation and a PF₆⁻ anion (Fig. 2), and for compound **4**·2CHBr₃ (triclinic space group $P\overline{1}$), it consists of a $[CuBrL]^+$ cation, a Br₃⁻ anion and two CHBr₃ molecules of crystallisation, all in general positions (Fig. 3).



Fig. 1. Perspective drawing of the compound $[CuBrL]_2[Cu_2Br_4]$ (1) showing the atom numbering. Thermal ellipsoids are drawn at the 50% probability level.



Fig. 2. ORTEP representation of the asymmetric unit for compound [CuClL]PF₆ (3). Thermal ellipsoids are drawn at the 50% probability level.



Fig. 3. ORTEP representation of the asymmetric unit for compound [CuBrL]Br₃ (4). Thermal ellipsoids are drawn at the 50% probability level.

The principal bond lengths and angles for the $[CuXL]^+$ cations of 1, 3 and 4 are listed in Table 2. Obviously, these three cations present similar features with an essentially planar CuN₃X co-ordination polyhedron of the copper(II) atom (Table 2). Note, however, that if in 1 the N_3X tetra-atomic system is exactly planar, it exhibits a slight butterfly-like deformation in 3 and 4. Although the ML fragment is not bisected by a crystallographic mirror plane, the two halves of the co-ordinated ligand exhibit almost similar metric features and therefore the [CuXL]⁺ cation may reach the $C_{\rm s}$ or even higher C_{2v} molecular symmetry (Table 2). The bond angle values around the metal atom, in the range 78-102°, are indicative of strong distortions of the co-ordination polyhedron, with respect to the square, arising from the bite of the terdentate ligand. The metal-ligand bond lengths, which include Cu-N_{imine} bond distances somewhat longer than the Cu-N_{py} bond length, are usual and in good agreement whith those previously reported [4]. For instance, values observed for the Cu- N_{py} bond distances, labelled a in Table 2, fall in the range 1.913(7) - 1.938(5) Å; they are close to those observed for other Cu(II) complexes with almost similar organic ligands L' and L" such as $[CuL'(NO_3)_2]$ (1.913(3) Å) [4a] and $[CuL''_2](PF_6)_2$ (1.9419(11) and 1.9561(11) Å) [4b] (Scheme 1). As in these compounds, in complexes 1, 2 and 4, the C_{imine}-N_{imine} f bond lengths are significantly shorter (approximately 0.05 Å) than the C_{py} - N_{py} d distances, consistent with the double-bond character of the former (Table 2). The C_{py} - C_{imine} e bond lengths, and even those of C_{imine}-CH₃ g, are significantly shorter than

usual σ C–C bond distances. This indicates a high π electronic delocalisation within the terdentate ligand.

In compound 1, the centrosymmetric $[Cu_2Br_4]^{2-}$ anion is alike to those of the $[Me_3PhN]_2[Cu_2Br_4]$ and $[Et_4N]_2[Cu_2Br_4]$ salts previously described by Jagner et al. [11]. The copper(I) atoms co-ordination corresponds to a strongly distorted planar triangle characterised by Cu–Br distances varying from 2.325(2) to 2.400(2) Å (vs. 2.310(1)–2.417(1) Å in Me_3PhN salt, 2.319(2)– 2.454(2) Å in Et_4N salt and 2.337(2)–2.454(1) Å in the MePh_3P salt) and Br–Cu–Br angles in the range 114.26–123.62° (Table 3). However, the Cu(I)…Cu(I) distance 2.601(2) Å is clearly shorter than the corresponding values in these salts (2.937(3), 2.738(9) and 2.697(2) Å).

In compound 1, the short contact observed between the copper atom of the cation and one of the bromo ligand of the anion (Cu(1)…Br(2) 2.689(2) Å) corresponds to the well known tendency of square planar copper(II) to extend its co-ordination number up to five or even six [12]. As a result, the whole structure must be viewed as built of 'tetranuclear' units (Fig. 1).

In compound 3, the PF_6^- anion displays a regular octahedral geometry characterised by P–F distances in the range 1.590(2)–1.608(2) Å and F–P–F angles varying from 89.42(7) to 90.77(8)°. A weak interaction arises between the anion and the copper(II) atom as shown by the Cu…F(2) distance (2.645(2) Å).

In compound 4, the Br_3^- anion is almost linear (BrBrBr = 175.34(6)°) and symmetrical (BrBr 2.250(2) and 2.255(2) Å). It is well known that this anion, like the I_3^- anion, may be symmetrical or unsymmetrical

depending on its environment [13]. As in derivative **3** a weak interaction is observed between the anion and the copper(II) atom (Cu···Br(2) 3.141(2) Å).

3.3. Electrochemical studies

For complexes $[CuBrL]_2[Cu_2Br_4]$ (1), CuL(CH₃CN)(THF)PF₆ (2) and $[CuBrL]Br_3$ (4), cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry studies were performed in CH₃CN or THF in order to evaluate their redox behaviour; every attempt of characterisation of compound [CuClL]PF₆ (3) failed since decomposition occurred in any solvent tested.

For complexes 1 and 4, a typical voltammogram displays several redox processes as shown in Fig. 4. On the cathodic scan (E < -0.5 V), the electrode responses are ascribed to the reduction of Cu(I) to Cu(0) with copper deposit, as indicated by the redissolution

peak at -0.70 V [14]; furthermore, in the case of compound 4, the reduction peak of CHBr₃ is combined with the copper deposit peak. The redox processes located at potentials higher than 0.0 V correspond to the oxidation of Br^- or Br_3^- , and in the case of compound 1 also correspond to that of the $[Cu_2^I Br_4]^{2-}$ anionic species. This has been verified by independent CV but the exact assignation of theses processes has not been scrutinised. Therefore, the redox process comprised in both cases between -0.5 and 0.0 V corresponds to the Cu(II)/Cu(I) exchange for the [CuBrL]⁺ moiety (peaks A/A') (Fig. 4). The Cu(II) redox state in this moiety was emphasized by the reduction wave observed by rotating disk electrode voltammetry (not shown). The cyclic voltammograms (Figs. 4 and 5) were recorded starting from a potential more cathodic than the A/A' system (-0.5 V), thus the Cu(II) moiety was converted into the Cu(I) complex in the diffusion layer before the run. As exemplified in Fig. 5, at low scan

Table 2

 $[CuLX]^+$ cation in 1, 3 and 4: selected bond lengths a (Å), bond angles a (°) and planarity b



1			3		4	
Cu co-o	rdination					
a	1.938(5)		1.922(2)		1.913(7)	
b	2.071(5)	2.133(5)	2.070(2)	2.062(2)	2.067(6)	2.079(6)
с	2.328(2) °		2.1450(5) ^d		2.325(2) °	
α	78.4(2)	78.1(2)	79.14(6)	79.40(6)	79.7(3)	78.8(3)
β	99.6(2)	99.6(2)	101.74(5)	99.64(5)	101.0(2)	99.8(2)
Planarit	y and deviations ^b					
N1	0.001(2)		N1	0.0594(9)	N1	0.073(4)
N2	-0.001(3)		N2	-0.0480(7)	N2	-0.058(3)
N3	-0.001(2)		N3	-0.0476(7)	N3	-0.057(3)
Br1	0.001(2)		Cl	0.0361(5)	Br1	0.041(2)
Cu	0.292(2)		Cu	0.0609(7)	Cu	0.130(3)
Br2	2.956(3)		F2	2.674(2)	Br2	3.182(3)
L ligana	l					
d	1.316(8)	1.336(8)	1.335(2)	1.333(2)	1.325(9)	1.36(1)
е	1.460(9)	1.467(9)	1.495(2)	1.483(2)	1.50(2)	1.48(1)
f	1.287(8)	1.273(8)	1.285(3)	1.294(2)	1.28(1)	1.30(2)
g	1.486(9)	1.483(9)	1.492(3)	1.484(3)	1.49(1)	1.51(2)
h	1.449(8)	1.452(8)	1.446(2)	1.447(2)	1.439(9)	1.431(9)
χ	118.1(4)	118.6(4)	118.7(2)	118.8(2)	118.7(5)	120.1(5)
δ	113.2(6)	114.1(6)	112.8(2)	112.4(2)	110.9(6)	111.6(6)
З	115.9(6)	115.5(6)	115.3(2)	114.7(2)	115.0(6)	116.9(6)
γ	113.2(5)	113.7(4)	113.8(2)	114.7(2)	114.1(5)	112.9(5)
η	125.6(4)	126.7(4)	125.8(2)	122.8(2)	125.8(5)	126.7(5)

^a Since the ML fragment is not bisected by a crystallographic mirror plane, two values corresponding to the two halves of the ligand are given when appropriate.

 $^{\rm b}$ Distance of the atom from the mean plane $N_1N_2N_3X.$

 $^{c} X = Cl.$

^d X = Br.

Table 3

Selected bond lengths (Å) and bond angles (°) associated to the $[Cu_2Br_4]^{2-}$ anion and the anion–cation interactions in 1

Bond lengths			
Br(2)–Cu(2)	2.325(2)	Br(2)–Cu(1)	2.689(2)
Br(3)-Cu(2)	2.391(2)	$Cu(2)$ – $Br(3)^i$	2.400(2)
$Cu(2)$ – $Cu(2)^i$	2.601(2)		
Bond angles			
Br(2)-Cu(2)-Br(3)	122.09(5)	$Br(2)-Cu(2)-Br(3)^{i}$	123.62(5)
Cu(2)-Br(2)-Cu(1)	124.59(4)	$Cu(2)-Br(3)-Cu(2)^{i}$	65.74(4)
N(1)-Cu(1)-N(3)	78.4(2)	N(1)-Cu(1)-N(2)	78.1(2)
N(3)-Cu(1)-N(2)	153.2(2)	N(1)-Cu(1)-Br(1)	164.2(2)
N(3)-Cu(1)-Br(1)	99.6(2)	N(2)-Cu(1)-Br(1)	99.6(2)
N(1)-Cu(1)-Br(2)	91.7(2)	N(3)-Cu(1)-Br(2)	100.1(2)
N(2)-Cu(1)-Br(2)	93.1(2)	Br(1)-Cu(1)-Br(2)	104.15(4)
$Br(3)-Cu(2)-Br(3)^{i}$	114.26(4)	$Br(2)-Cu(2)-Cu(2)^{i}$	178.13(6)
$Br(3)-Cu(2)-Cu(2)^{i}$	57.30(4)	$Br(3)^i$ -Cu(2)-Cu(2) ⁱ	56.95(4)

Symmetry transformation used to generate equivalent atoms: (i): -x, -y+1, -z+1.



Fig. 4. Cyclic voltammogram of compound 1 (approximately 10^{-3} M in MeCN, 0.2 M Bu₄NPF₆, platinum electrode, scan rate 0.1 V s⁻¹).

rate, v, (up to v = 0.1 V s⁻¹), a single reversible redox process is seen (peaks A/A': $E'^{\circ}(1) = -0.24$ V; $\Delta E_{\rm p} =$ 140 mV; $i_{\rm pa}/i_{\rm pc} \approx 1$) for both compounds 1 and 4; at higher scan rates, (0.2 < v < 1.0 V s⁻¹), the peaks intensity of process A/A' decreases giving rise to another reversible redox process (peaks B/B': $E'^{\circ}(2) = -0.08$ V; $\Delta E_{\rm p} = 120$ mV). This scan rate dependent behaviour appears typical of a CE process, for which we propose the following square scheme involving equilibria between bromo and non-bromo Cu^IL and Cu^{II}L species (Scheme 3):



Along with this scheme, at the starting potential, [Cu^IBrL] would be in equilibrium with the unbrominated species $[Cu^{I}L]^{+}$; while at high scan rate the oxidation of both species in equilibrium can be seen (systems A/A' and B/B'), at lower scan rate only the easiest oxidation of $[Cu^{I}BrL]$ into $[Cu^{II}BrL]^{+}$ at $E'^{\circ}(2)$ can be observed via the CE process. This interpretation is corroborated by the observation that the peak of the second process disappears in the presence of an excess of Br⁻ anion in the same conditions for CV. A higher stability of the $[Cu^{II}BrL]^{+}$ derivative as compared to $[Cu^{I}BrL]$ can be easily rationalised both in terms of charge stabilisation and Cu co-ordination (square vs. tetrahedral).

The Cu(I) compound CuL(CH₃CN)(THF)PF₆ (**2**) is quite unstable in acetonitrile in which decomplexation of the L ligand occurs very quickly; however, this complex could be electrochemically characterised in THF. The corresponding CV displays two quite close redox processes, one pseudo-reversible for the oxidation of Cu(I) ($E'^{\circ} = +0.23$ V; $\Delta E_{\rm p} = 190$ mV), the other irreversible at $E_{\rm p}$ (red) = -0.07 V to the reduction of Cu(I) into Cu(0) with deposit.

3.4. Discussion

As reported above, the three new Cu(II) complexes 1, 3 and 4, which have been fully characterised by X-ray crystal structure determinations, are prepared from Cu(I) starting materials.

Reproductive formation of 1 in a rather good yield by reaction of CuBr with the ligand in THF, thus by concomitant oxidation of the copper(I), is not explained away since (i) the starting THF solution of CuBr is pure as regard to copper(II) (ESR) with only traces of paramagnetism; (ii) the synthesis was performed under oxygen free atmosphere; (iii) the ligand and the solvent do not possess significant oxidant properties; and (iv) no trace of metallic copper indicative of a dismutation process was found.



Fig. 5. Cyclic voltammograms of compound 1 at different scan rates (a: v = 0.1, b: v = 0.2, c: v = 0.5, d: v = 1.0 V s⁻¹).

For both compounds **3** and **4**, the formation of a copper(II) complex results from an halogen atom transfer from an halogenated solvent to a copper(I) species. It seems likely that these reactions proceed via a radical mechanism [15] considering the previously reported formation of the copper(II) derivative [Cu(AA)₂Br]PF₆) (AA = 4,4'-(5-nonyl)-2,2'-bipyridine) by reaction at r.t. in acetonitrile between the copper(I) complex [Cu(AA)₂]PF₆ and one equivalent of CHBr₃. On the other hand, formation of the tribromide Br₃⁻ anion in **4** with bromoform as the only source of bromine is quite unexpected.

The crystal structure of 1 (despite the anion-cation short contact via a Br bridge), its magnetic properties and colour clearly show that, as a mixed valence Cu(I)-Cu(II) complex, this compound belongs to the class I of the Robin and Day classification [16].

Previous studies have shown that the $[Cu_2Br_4]^2$ anion is capable of considerable flexibility with respect to its geometry under different steric and electrostatic constraints in the solid state [11]. As far as we know, the Cu(I)…Cu(I) distance in 1 (2.601(2) Å) is the shortest ever seen for this anion. However, much shorter Cu(I)…Cu(I) distances have been previously reported for instance in the trinuclear complex [Cu₃(RN₅R)₃] (R: PhMe) (2.348(2) and 2.358(2) Å) [17].

4. Supplementary material

Full crystallographic data for reported complexes have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 162614-162616 for compounds [CuBrL]₂[Cu₂Br₄] (1), [CuClL]Pf₆ (3), [Cu-ClL]Br₃ (4) respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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