

# Crystal Structure and Spectroscopic and Magnetic Properties of Two Novel Mono( $\mu$ -halo) Copper(II) Chains with an Unusual Zigzag Arrangement: $[\text{Cu}(\text{C}_{13}\text{H}_{13}\text{N}_3)\text{X}]\text{PF}_6$ ( $\text{X} = \text{Cl}, \text{Br}$ )

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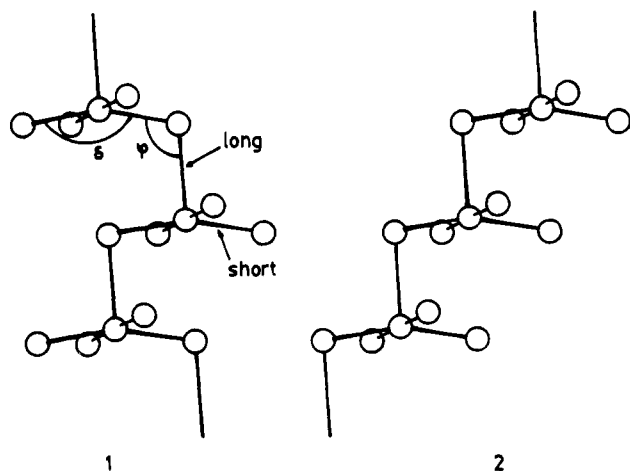
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Three new compounds  $[\text{Cu}(\text{C}_{13}\text{H}_{13}\text{N}_3)\text{Cl}](\text{PF}_6)_n\text{H}_2\text{O}$  [ $n = 1$  (**1**);  $n = 0$  (**2**)] and  $[\text{Cu}(\text{C}_{13}\text{H}_{13}\text{N}_3)\text{Br}](\text{PF}_6)$  (**3**), where  $\text{C}_{13}\text{H}_{13}\text{N}_3 = \text{pepci} = N$ -(2-pyridylethyl)pyridine-2-carbaldimine, have been synthesized and the crystal structures of **2** and **3** determined at room temperature. Both compounds crystallize in the orthorhombic system, space group  $Pc2_1b$  and  $Z = 16$ , with cell parameters of  $a = 7.804(2)$  Å,  $b = 24.686(4)$  Å,  $c = 34.376(9)$  Å, and  $V = 6623(3)$  Å<sup>3</sup> for compound **2** and  $a = 7.904(3)$  Å,  $b = 24.816(3)$  Å,  $c = 34.289(4)$  Å, and  $V = 6726(3)$  Å<sup>3</sup> for compound **3**. The structure of **2** was refined to an  $R$  value of 0.068 ( $R_w = 0.055$ ), while the structure of **3** was refined to  $R = 0.071$  ( $R_w = 0.067$ ). Both structures consist of  $[\text{Cu}(\text{pepci})\text{X}]^+$  ( $\text{X} = \text{Cl}, \text{Br}$ ) cations which stack along the  $a$  axes and  $\text{PF}_6^-$  anions sited in the interchain space. In the stack, two successive copper complexes are in an alternating orientation, to give a novel zigzag mono( $\mu$ -halide) chain structure. There are four independent  $[\text{Cu}(\text{pepci})\text{X}](\text{PF}_6)$  molecules in the unit cell, which are repeated four times. The chloro compounds **1** and **2** are not isostructural phases, compound **1** being characterized as a dimer. Magnetic properties of the compounds have been investigated down to 4 K. The chloro complexes exhibit weak antiferromagnetic interactions, while the bromo one is ferromagnetic. The magnetic susceptibility data for both chains (**2** and **3**) have been fitted by using a linear chain model. The obtained parameters are  $J/k = -2.0$  K ( $1.39$  cm<sup>-1</sup>) (**2**) and  $J/k = +1$  K ( $0.70$  cm<sup>-1</sup>) (**3**). However, the data corresponding to complex **1** have been fitted to a dimer system, with an exchange coupling constant of  $-3.0$  K ( $2.09$  cm<sup>-1</sup>). Magneto-structural correlations in the chloro-bridged chains have been analyzed by using extended Hückel molecular orbital calculations.

## Introduction

The low-dimensional magnetic systems of transition-metal ions represent an area of great interest for both physicists and chemists due to the peculiar behaviors derived from the nature of those magnetic ions. The study of the structure and magnetic exchange interactions in these kinds of compounds is aimed to the understanding of the structural and chemical features that govern the magnitude and sign of the exchange coupling constants (magneto-structural correlations).<sup>1,2</sup>

The pentacoordinated mono( $\mu$ -halo)-bridged copper(II) chains, which exhibit  $\text{CuY}_3(\mu\text{-X})$  cores as repeating units, represent a particular case of these 1D systems. The long Cu-X bonds occupy either the apical position in a square pyramid or one of the equatorial sites of a trigonal bipyramid.<sup>3-6</sup> Two configurations are possible for these monobridged chains:



The geometrical parameters defining these kinds of structures are the  $\delta$  angle ( $180^\circ$  for the square pyramid and  $120^\circ$  for the trigonal bipyramid) and the bridging angle  $\varphi$ , experimentally varying from  $114$  to  $145^\circ$ . Though a certain number of monochloro-bridged chains is known,<sup>3-5</sup> the monobromo-bridged chains are very scarce, being of great interest both their preparation and the study of magneto-structural correlations.

The quasi-planar tridentate ligands ( $\text{L}_{\text{M}}$ ) are able to generate  $[\text{ML}_{\text{M}}\text{X}]^+$  species, whose stacking gives rise to polynuclear entities (dimers or chains). In the last years, a synthetic strategy has been developed by our group to obtain copper(II) 1D systems with tridentate ligands of general formula  $[\text{Cu}(\text{L}_{\text{M}})\text{XY}]$  ( $\text{X} = \text{halide}$  or pseudohalide,  $\text{Y} = \text{coordinating}$  or noncoordinating anion). In this way, classic and ladder-like chains and dimers<sup>7-9</sup> have been obtained showing that the nature of the tridentate ligands is a determining factor governing the structure of the polynuclear systems. As a result, the use of extremely rigid ligands like terpy ( $2,2':6',2''$ -terpyridine) has led to the obtention of dimeric molecules,<sup>7,8</sup> while with other less rigid tridentate ligands, chain structures are obtained.<sup>9</sup> To corroborate these trends and to obtain mono( $\mu$ -halo)-bridged chains, we have used the new more flexible "pepci" ligand [ $N$ -(2-pyridylethyl)pyridine-2-carbaldimine] and synthesized the  $[\text{Cu}(\text{pepci})\text{X}](\text{PF}_6)_n\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}; n = 0, 1$ ) compounds.

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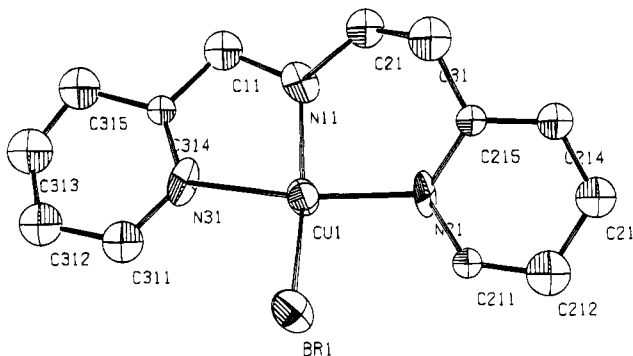
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**Table 1.** Crystallographic Data for [Cu(pepci)X](PF<sub>6</sub>) (X = Cl (2), Br (3))

	2	3
chem formula	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> CuClPF <sub>6</sub>	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> CuBrPF <sub>6</sub>
<i>a</i> , Å	7.804(2)	7.904(3)
<i>b</i> , Å	24.686(4)	24.816(3)
<i>c</i> , Å	34.376(9)	34.289(4)
<i>V</i> , Å <sup>3</sup>	6623(3)	6726(3)
<i>Z</i>	16	16
fw	455.23	499.68
space group	<i>Pc2<sub>1</sub>b</i> (No. 29)	<i>Pc2<sub>1</sub>b</i> (No. 29)
<i>T</i> , °C	25	25
$\lambda$ , Å	0.710 69	0.710 69
$\rho_{\text{obsd}}$ , g cm <sup>-3</sup>	1.80(2)	1.97(2)
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.82	1.97
$\mu$ , cm <sup>-1</sup>	17.12	38.12
$R(F_o)^a$	0.068	0.071
$R_w(F_o)^b$	0.055	0.067

<sup>a</sup>  $R(F_o) = (\sum ||F_o| - |F_c||) / (\sum |F_o|)$ . <sup>b</sup>  $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ .

**Figure 1.** Perspective view of the [Cu(pepci)X]<sup>+</sup> (X = Cl, Br) entities which stack to generate the polynuclear compounds.

In this work the crystal structures of two new mono( $\mu$ -chloro) and mono( $\mu$ -bromo) copper(II) chain compounds and their magnetic properties are reported. A related hydrated chloride compound has also been synthesized and studied.

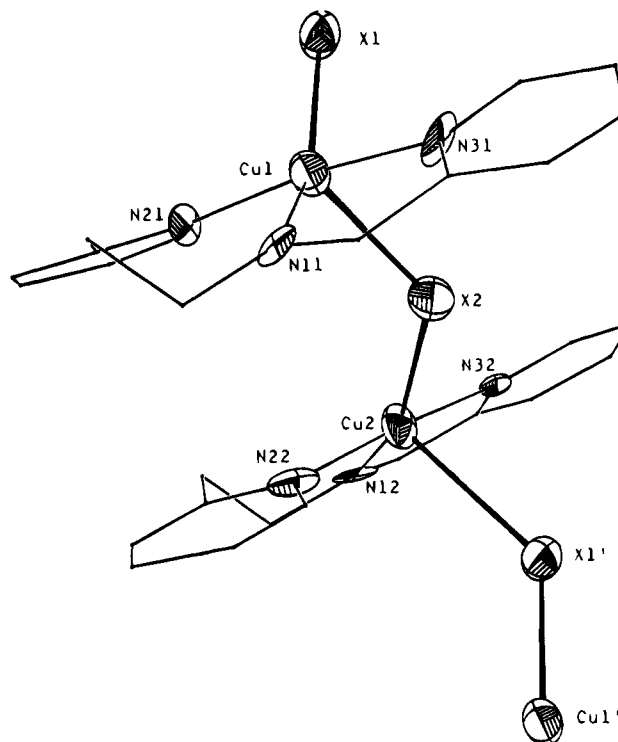
## Experimental Section

**Compound Preparations.** All materials used in this work were of reagent grade purity and were used as commercially obtained. The pepci ligand was prepared by condensation of 2-pyridinecarboxaldehyde and (2-aminoethyl)pyridine. The chloro [Cu(pepci)(H<sub>2</sub>O)Cl](PF<sub>6</sub>)·H<sub>2</sub>O (1) and the bromo [Cu(pepci)Br]PF<sub>6</sub> (3) complexes were prepared by following the same method. An excess of potassium hexafluorophosphate was added to both aqueous solutions (0.100 g in 25 mL) of Cu(pepci)Cl<sub>2</sub>·H<sub>2</sub>O and Cu(pepci)Br<sub>2</sub>·H<sub>2</sub>O complexes, previously prepared by mixing equimolar amounts of CuX<sub>2</sub>·*n*H<sub>2</sub>O (X = Cl, Br) and the pepci ligand. The resulting blue precipitates were filtered off, washed with water, and dried over P<sub>2</sub>O<sub>5</sub> for 48 h. Compound 2 was obtained by recrystallization of complex 1 in an acetone solution. Crystals of 3 were obtained by slow evaporation of a water/acetone solution of the previously prepared precipitate. All the attempts to obtain good quality crystals of compound 1 were not successful.

The analyses of the compounds were consistent with the formulas C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>ClCuPF<sub>6</sub>·H<sub>2</sub>O, C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>ClCuPF<sub>6</sub>, and C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>BrCuPF<sub>6</sub> for 1–3, respectively.

**Physical Measurements.** Elemental analyses (C, H, N) were performed with a Perkin-Elmer Model 240 automatic analyzer. IR spectra were recorded for KBr disks on a Perkin-Elmer 1720X FT-IR spectrophotometer in the 4000–400 cm<sup>-1</sup> region.

Magnetic susceptibilities of powdered samples of the title complexes were determined with a SQUID SHE magnetometer, working at 0.2 T. The measurements were performed in the 4–300 K temperature range. The susceptibilities per mole of the copper ions were corrected for diamagnetism from Pascal's tables, and the temperature-independent paramagnetism was estimated to be +60 × 10<sup>-6</sup> cm<sup>3</sup>/mol of copper

**Figure 2.** ORTEP view of one of the two crystallographically independent fragments for both [Cu(pepci)Cl](PF<sub>6</sub>) (2) and [Cu(pepci)Br](PF<sub>6</sub>) (3).

ion. EPR spectra of powdered samples were recorded with a Bruker ESP 300 spectrometer, equipped with a standard Oxford low-temperature device, operating at X-band, calibrated by the NMR probe for the magnetic field and a Hewlett Packard 5352B frequency counter for the microwave frequency.

**X-ray Structural Analyses of [Cu(pepci)X]PF<sub>6</sub> (X = Cl, Br).** X-ray quality blue needles of both 2 and 3 were obtained as described earlier in this section and mounted on glass capillaries. Diffraction experiments were performed on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation at room temperature, as summarized in Table 1. Preliminary cell dimensions were measured by oscillation and Weissenberg photographs. Final lattice parameters and orientation matrixes were determined by 25 reflections in the  $2\theta$  range  $6.54^\circ < 2\theta < 15.62^\circ$ . The observed systematic extinctions (and those extracted from the Weissenberg photographs as well) were consistent in both cases with the space group *Pc2<sub>1</sub>b*. Three standard reflections were monitored every 2 h and showed good stabilities over the duration of data collection. Intensity data were corrected for Lorentz and polarization effects, but no absorption correction was applied. The data were processed by using the X-Ray-72 System program package.<sup>10</sup> A total of 1878 (2) and 2405 (3) observed reflections with  $I \geq 3\sigma(I)$  were used for the structural determinations. The structure of 3 was solved using the SIR88<sup>11</sup> program, which was able to handle properly the strong pseudotranslational effect present in the collected set of reflections. The corresponding structure of compound 2 was obtained from the isostructural complex 3. In both cases the refinement was carried out by full-matrix least-squares techniques to the final reliability factors  $R = 0.068$  and  $R_w = 0.055$  for 2 and  $R = 0.071$  and  $R_w = 0.067$  for 3 (the weights were taken as  $w = 1/[\sigma(F)^2]$ ). Anisotropic temperature factors were assigned to all non-hydrogen, non-carbon, and non-nitrogen atoms in compound 2, while for compound 3 anisotropic temperature factors were assigned to all non-hydrogen, non-carbon, and

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**Table 2.** Positional and Isotropic Equivalent Thermal Parameters for [Cu(C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>)Cl](PF<sub>6</sub>) (2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq), <sup>a</sup> Å <sup>2</sup>		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq), <sup>a</sup> Å <sup>2</sup>
Cu1	0.3443(4)	0.4558(1)	0.44883(8)	0.038(1)	C332	0.293(3)	0.2788(9)	0.1832(7)	0.044(7)
Cl1	0.1430(9)	0.3899(2)	0.4458(2)	0.053(3)	C333	0.271(3)	0.231(1)	0.1604(6)	0.054(7)
N11	0.443(2)	0.5338(7)	0.4450(5)	0.029(5)	C334	0.252(3)	0.1812(9)	0.1804(7)	0.044(7)
C11	0.467(3)	0.547(1)	0.4104(7)	0.043(7)	C335	0.255(3)	0.1819(9)	0.2204(6)	0.032(7)
C21	0.479(3)	0.569(1)	0.4800(8)	0.059(8)	Cu4	0.7728(4)	0.3220(1)	0.26401(8)	0.037(1)
C31	0.328(3)	0.5599(9)	0.5081(6)	0.038(7)	Cl4	0.5764(8)	0.2909(3)	0.3062(2)	0.047(3)
N21	0.353(3)	0.4597(8)	0.5067(5)	0.045(5)	N14	-0.140(3)	0.3720(8)	0.2216(5)	0.045(6)
C211	0.364(4)	0.410(1)	0.5253(7)	0.040(8)	Cl4	-0.108(3)	0.4188(9)	0.2302(7)	0.030(7)
C212	0.370(4)	0.404(1)	0.5657(8)	0.066(9)	C24	-0.137(3)	0.353(1)	0.1811(7)	0.038(7)
C213	0.368(3)	0.455(1)	0.5887(7)	0.048(7)	C34	-0.270(3)	0.3158(8)	0.1727(5)	0.019(5)
C214	0.359(4)	0.504(1)	0.5689(8)	0.061(8)	N24	-0.185(2)	0.3926(6)	0.2950(5)	0.028(5)
C215	0.337(3)	0.5067(9)	0.5290(6)	0.032(6)	C241	-0.193(3)	0.3991(8)	0.3333(6)	0.028(6)
N31	0.357(3)	0.4618(8)	0.3886(5)	0.045(6)	C242	-0.138(3)	0.446(1)	0.3515(6)	0.039(7)
C311	0.321(4)	0.421(1)	0.3627(8)	0.061(8)	C243	-0.083(3)	0.492(1)	0.3291(8)	0.054(8)
C312	0.359(3)	0.4313(9)	0.3233(6)	0.036(7)	C244	-0.074(3)	0.484(1)	0.2874(8)	0.058(9)
C313	0.419(3)	0.481(1)	0.3134(7)	0.045(7)	C245	-0.121(3)	0.4359(9)	0.2709(6)	0.027(7)
C314	0.431(3)	0.5086(9)	0.3787(6)	0.034(6)	N43	-0.230(2)	0.2583(7)	0.2283(5)	0.026(5)
C315	0.460(4)	0.520(1)	0.3380(8)	0.062(9)	C341	-0.210(2)	0.2129(8)	0.2485(6)	0.021(6)
Cu2	0.8418(4)	0.3591(1)	0.48597(8)	0.042(1)	C342	-0.205(3)	0.1589(8)	0.2310(6)	0.036(7)
Cl2	0.6453(9)	0.3946(3)	0.4442(2)	0.053(3)	C343	-0.224(3)	0.1615(9)	0.1873(7)	0.044(7)
N12	-0.063(2)	0.3122(7)	0.5298(5)	0.035(5)	C344	-0.243(3)	0.2103(8)	0.1703(6)	0.032(6)
Cl2	-0.049(3)	0.260(1)	0.5201(7)	0.048(8)	C345	-0.244(3)	0.2593(7)	0.1905(5)	0.019(6)
C22	-0.043(3)	0.3329(8)	0.5696(6)	0.015(6)	P1	-0.005(1)	0.1045(4)	0.0847(3)	0.048(4)
C32	-0.181(3)	0.371(1)	0.5797(7)	0.054(8)	F11	0.039(2)	0.1630(7)	0.5973(5)	0.070(8)
N22	-0.145(2)	0.4269(6)	0.5184(5)	0.023(5)	F12	-0.099(3)	0.0920(8)	0.6224(6)	0.10(1)
C221	-0.161(4)	0.286(1)	0.4185(9)	0.08(1)	F13	-0.034(2)	0.0458(6)	0.5719(5)	0.068(8)
C222	-0.143(3)	0.232(1)	0.4022(7)	0.058(8)	F14	0.116(3)	0.1128(9)	0.5496(7)	0.14(1)
C223	-0.084(4)	0.192(1)	0.426(1)	0.09(1)	F15	0.163(3)	0.086(1)	0.6061(7)	0.12(1)
C224	-0.043(3)	0.1976(9)	0.4646(7)	0.038(7)	F16	-0.151(3)	0.1207(8)	0.5646(7)	0.13(1)
C225	-0.080(4)	0.251(1)	0.4769(8)	0.054(9)	P2	-0.113(1)	0.0798(4)	0.3339(3)	0.045(4)
N32	-0.137(3)	0.2907(8)	0.4562(6)	0.049(6)	F21	0.076(2)	0.1424(7)	0.8217(6)	0.081(9)
C321	-0.127(3)	0.4755(9)	0.5011(6)	0.039(8)	F22	0.001(2)	0.0620(7)	0.7972(6)	0.089(9)
C322	-0.121(3)	0.0234(9)	0.9774(6)	0.033(6)	F23	0.142(2)	0.0182(7)	0.8448(4)	0.081(8)
C323	-0.130(4)	0.523(1)	0.5598(7)	0.052(8)	F24	0.273(3)	0.0805(9)	0.8045(6)	0.13(1)
C324	-0.149(4)	0.472(1)	0.5817(7)	0.068(9)	F25	0.221(2)	0.0994(8)	0.8668(5)	0.11(1)
C325	-0.164(3)	0.4253(9)	0.5583(7)	0.042(7)	F26	-0.051(3)	0.0836(9)	0.8588(7)	0.11(1)
Cu3	0.2732(4)	0.2259(1)	0.29955(8)	0.036(1)	P3	0.535(1)	0.2386(4)	0.0490(3)	0.046(3)
Cl3	0.0746(9)	0.2929(3)	0.3043(2)	0.053(3)	F31	0.405(2)	0.7063(8)	0.4739(7)	0.10(1)
N13	0.360(2)	0.1511(6)	0.3032(5)	0.025(5)	F32	0.545(2)	0.6893(7)	0.4216(5)	0.073(8)
Cl3	0.393(3)	0.1294(9)	0.3363(7)	0.026(7)	F33	0.517(2)	0.7873(8)	0.4782(6)	0.10(1)
C23	0.373(3)	0.1133(8)	0.2682(6)	0.023(6)	F34	0.384(3)	0.7642(9)	0.4265(5)	0.13(1)
C33	0.226(3)	0.1275(8)	0.2433(6)	0.031(6)	F35	0.677(2)	0.7706(8)	0.4268(6)	0.11(1)
N23	0.317(2)	0.2218(7)	0.3575(4)	0.029(5)	F36	0.681(2)	0.7138(9)	0.4769(6)	0.12(1)
C231	0.298(3)	0.265(1)	0.3849(7)	0.056(8)	P4	0.378(1)	0.4454(3)	0.1976(3)	0.050(4)
C232	0.347(3)	0.2538(9)	0.4233(7)	0.045(7)	F41	0.383(3)	0.3959(7)	0.2287(5)	0.11(1)
C233	0.403(3)	0.202(1)	0.4339(7)	0.056(9)	F42	0.262(2)	0.4771(6)	0.2274(4)	0.050(6)
C234	0.425(3)	0.159(1)	0.4083(7)	0.037(8)	F43	0.494(3)	0.4144(8)	0.1661(6)	0.11(1)
C235	0.373(3)	0.1723(9)	0.3662(7)	0.042(7)	F44	0.222(3)	0.4207(9)	0.1762(6)	0.13(1)
N33	0.271(2)	0.2247(7)	0.2420(5)	0.035(5)	F45	0.372(2)	0.4954(6)	0.1686(5)	0.069(7)
C331	0.286(3)	0.2752(9)	0.2240(6)	0.027(7)	F46	0.540(2)	0.4713(8)	0.2189(6)	0.09(1)

$$^a U(\text{eq}) = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i a_j$$

non-fluorine atoms. Atomic scattering factors were taken from ref 12. No attempt was made to locate H atoms. The final difference Fourier synthesis was featureless. Positional parameters for independent atoms of the two complexes are given in Tables 2 and 3. Thermal parameters and complete bond distances and angles have been deposited as supplementary material.

## Results and Discussion

**Structures of [Cu(pepci)X]<sub>n</sub>(PF<sub>6</sub>)<sub>n</sub> (X = Cl, Br).** The crystal structures of both compounds **2** and **3** consist of cationic [Cu(pepci)X]<sup>+</sup> (X = Cl, Br) units (Figure 1) and PF<sub>6</sub><sup>-</sup> anions. These cationic units are bridged by X<sup>-</sup> anions to give a novel zigzag polymeric chain structure in the lattice. Two crystallographically independent consecutive [Cu(pepci)X]<sup>+</sup> cations are present in each chain. These double entities repeat by translation to give the chain structure along the *a* axis. In the unit cell four independent [Cu(pepci)X](PF<sub>6</sub>) units exist (each of them

repeated four times: *Z* = 16). The hexafluorophosphate ions are isolated in the interchain space. An ORTEP<sup>13</sup> drawing of one of the repeating units for both compounds is shown in Figure 2. Selected interatomic dimensions are given and compared in Table 4. The mono(*μ*-halide)-bridged chain structure is shown, by means of a SCHAKAL<sup>14</sup> drawing, in Figure 3.

The disposition of donor atoms around the copper(II) ions can be described as a distorted square-pyramidal geometry. The bridging halide ion occupies a basal position (where the Cu-Cl<sub>basal</sub> distances range from 2.245(7) to 2.276(7) Å and the Cu-Br<sub>basal</sub> ones from 2.382(3) to 2.434(3) Å) in the distorted square-pyramidal copper(II) and an axial position (where Cu-Cl<sub>apical</sub> distances range from 2.797(8) to 2.868(7) Å and Cu-Br<sub>apical</sub> ones between 2.856(3) and 2.888(3) Å) in the adjacent

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**Table 3.** Positional and Isotropic Equivalent Thermal parameters for [Cu(C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>)Br](PF<sub>6</sub>) (3)

	x	y	z	U(eq), <sup>a</sup> Å <sup>2</sup>		x	y	z	U(eq), <sup>a</sup> Å <sup>2</sup>
Cu1	0.3563(3)	0.4570(1)	0.44627(7)	0.0371(9)	C332	0.301(3)	0.2783(8)	0.1842(6)	0.032(6)
Br1	0.1451(3)	0.3860(1)	0.44077(7)	0.0444(9)	C333	0.275(3)	0.2323(9)	0.1648(6)	0.033(6)
N11	0.438(2)	0.5340(6)	0.4456(5)	0.036(7)	C334	0.263(3)	0.1839(9)	0.1834(7)	0.047(7)
C11	0.474(3)	0.5566(9)	0.4078(7)	0.044(6)	C335	0.273(3)	0.1790(8)	0.2233(6)	0.042(6)
C21	0.465(3)	0.5698(8)	0.4777(6)	0.043(7)	Cu4	0.8022(3)	0.3256(1)	0.26556(7)	0.0360(9)
C31	0.311(3)	0.5583(9)	0.5071(6)	0.051(7)	Br4	0.5947(3)	0.2925(1)	0.31157(6)	0.0457(8)
N21	0.355(2)	0.4580(7)	0.5046(4)	0.038(6)	N14	-0.119(2)	0.3742(7)	0.2204(4)	0.036(7)
C211	0.374(2)	0.4118(7)	0.5249(5)	0.025(5)	C14	-0.084(2)	0.4220(8)	0.2283(5)	0.022(5)
C212	0.370(3)	0.4045(8)	0.5638(6)	0.056(7)	C24	-0.118(2)	0.3511(8)	0.1799(5)	0.033(6)
C213	0.341(3)	0.4544(8)	0.5862(6)	0.045(6)	C34	-0.260(3)	0.3131(8)	0.1729(6)	0.033(6)
C214	0.321(3)	0.5042(8)	0.5664(6)	0.036(6)	N24	-0.166(2)	0.3936(6)	0.2923(4)	0.037(6)
C215	0.337(2)	0.5057(7)	0.5269(5)	0.026(5)	C241	-0.176(2)	0.4038(7)	0.3345(6)	0.032(5)
N31	0.386(2)	0.4684(7)	0.3889(5)	0.042(7)	C242	-0.124(3)	0.4510(9)	0.3491(6)	0.043(6)
C311	0.354(3)	0.4291(9)	0.3600(6)	0.047(6)	C243	-0.063(3)	0.498(1)	0.3242(8)	0.079(9)
C312	0.390(3)	0.4414(9)	0.3202(6)	0.052(7)	C244	-0.058(2)	0.4865(8)	0.2831(5)	0.019(5)
C313	0.459(3)	0.4910(9)	0.3135(7)	0.059(7)	C245	-0.105(3)	0.4343(8)	0.2744(6)	0.028(5)
C314	0.441(2)	0.5169(8)	0.3779(6)	0.024(5)	N43	-0.201(2)	0.2618(7)	0.2336(5)	0.037(7)
C315	0.477(3)	0.5327(9)	0.3374(7)	0.050(7)	C341	-0.180(3)	0.2150(8)	0.2499(6)	0.040(6)
Cu2	0.8535(3)	0.3565(1)	0.48561(6)	0.0370(9)	C342	-0.184(3)	0.1645(7)	0.2306(5)	0.031(6)
Br2	0.6464(3)	0.3890(1)	0.44011(7)	0.0484(9)	C343	-0.210(3)	0.1631(9)	0.1914(7)	0.056(7)
N12	-0.069(2)	0.3118(6)	0.5287(5)	0.029(6)	C344	-0.229(3)	0.2123(9)	0.1736(6)	0.039(6)
C12	-0.049(3)	0.2650(8)	0.5213(6)	0.029(6)	C345	-0.232(2)	0.2612(8)	0.1949(6)	0.029(6)
C22	-0.045(2)	0.3311(7)	0.5699(5)	0.024(5)	P1	-0.0099(9)	0.1061(3)	0.0849(2)	0.043(3)
C32	-0.193(3)	0.3695(8)	0.5770(6)	0.048(7)	F11	0.033(2)	0.1660(6)	0.5975(4)	0.067(4)
N22	-0.145(2)	0.4255(6)	0.5168(4)	0.034(6)	F12	-0.093(2)	0.0960(7)	0.6247(5)	0.106(6)
C221	-0.142(3)	0.2740(8)	0.4207(6)	0.035(6)	F13	-0.023(2)	0.0430(6)	0.5742(4)	0.066(5)
C222	-0.116(3)	0.2210(9)	0.4046(6)	0.055(7)	F14	0.138(2)	0.1133(8)	0.5538(6)	0.120(7)
C223	-0.052(3)	0.181(1)	0.4290(8)	0.064(8)	F15	0.167(2)	0.0843(8)	0.6122(6)	0.121(7)
C224	-0.034(3)	0.1956(9)	0.4696(7)	0.058(7)	F16	-0.145(2)	0.1238(6)	0.5625(5)	0.093(5)
C225	-0.068(3)	0.2456(8)	0.4831(6)	0.035(6)	P2	-0.0974(9)	0.0782(3)	0.3374(2)	0.047(3)
N32	-0.124(2)	0.2872(6)	0.4578(4)	0.025(5)	F21	0.066(2)	0.1359(8)	0.8256(5)	0.101(6)
C321	-0.128(3)	0.4727(8)	0.4985(5)	0.030(5)	F22	-0.019(2)	0.0589(6)	0.7987(4)	0.071(4)
C322	-0.131(3)	0.0246(8)	0.9850(6)	0.040(6)	F23	0.129(2)	0.0183(6)	0.8486(4)	0.072(4)
C323	-0.151(3)	0.5240(9)	0.5599(7)	0.060(7)	F24	0.256(2)	0.0753(8)	0.8064(6)	0.127(7)
C324	-0.163(2)	0.4767(7)	0.5765(5)	0.033(5)	F25	0.209(2)	0.0985(7)	0.8672(5)	0.093(6)
C325	-0.163(2)	0.4240(7)	0.5590(5)	0.029(5)	F26	-0.067(2)	0.0812(6)	0.8611(5)	0.082(5)
Cu3	0.3038(3)	0.2243(1)	0.30337(7)	0.0372(9)	P3	0.5349(8)	0.2397(3)	0.0524(2)	0.046(3)
Br3	0.0974(3)	0.2937(1)	0.30952(7)	0.0498(8)	F31	0.401(2)	0.7078(7)	0.4710(5)	0.083(5)
N13	0.388(2)	0.1508(6)	0.3080(5)	0.035(6)	F32	0.546(2)	0.6908(6)	0.4147(5)	0.080(5)
C13	0.407(2)	0.1288(7)	0.3389(6)	0.025(5)	F33	0.511(2)	0.7884(6)	0.4751(4)	0.065(4)
C23	0.391(3)	0.1143(9)	0.2685(7)	0.054(7)	F34	0.405(2)	0.7670(8)	0.4213(6)	0.124(7)
C33	0.249(2)	0.1268(8)	0.2462(5)	0.028(5)	F35	0.667(2)	0.7750(8)	0.4225(6)	0.135(7)
N23	0.345(2)	0.2171(6)	0.3612(5)	0.046(7)	F36	0.670(2)	0.7135(7)	0.4727(5)	0.110(6)
C231	0.327(3)	0.2574(7)	0.3884(5)	0.026(5)	P4	0.3932(9)	0.4444(3)	0.1947(2)	0.043(3)
C232	0.380(3)	0.2475(9)	0.4276(7)	0.060(7)	F41	0.395(2)	0.3962(8)	0.2258(6)	0.121(7)
C233	0.422(3)	0.192(1)	0.4391(8)	0.074(9)	F42	0.279(2)	0.4764(6)	0.2257(5)	0.083(5)
C234	0.443(3)	0.154(1)	0.4089(7)	0.060(8)	F43	0.508(2)	0.4116(7)	0.1665(5)	0.087(5)
C235	0.380(3)	0.1672(9)	0.3742(7)	0.046(6)	F44	0.234(2)	0.4205(7)	0.1767(5)	0.097(6)
N33	0.297(2)	0.2232(7)	0.2441(4)	0.048(7)	F45	0.390(2)	0.4923(6)	0.1673(4)	0.068(4)
C331	0.314(3)	0.2729(8)	0.2279(6)	0.045(7)	F46	0.550(3)	0.472(1)	0.2157(9)	0.18(1)

$$^a U(\text{eq}) = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i a_j$$

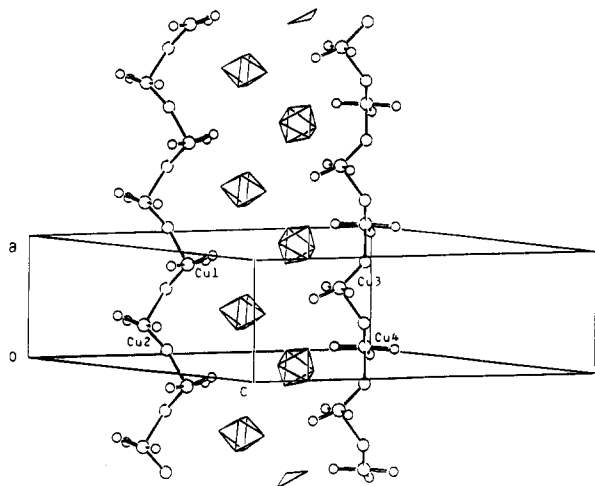
copper(II) environment (Figure 2), with alternating short and long distances. The three nitrogen atoms of the pepci ligand complete the basal sites in which the Cu–N distances range from 1.97(2) to 2.08(2) Å in the chloro chain and from 1.92(2) to 2.06(1) Å in the bromo chain. Deviations from square-pyramidal to trigonal-bipyramidal topologies have been calculated using the Muetterties<sup>15</sup> and Kepert<sup>16</sup> models. The data are compiled, with those corresponding to other related complexes, in the supplementary material. The title compounds are unique, showing a trigonally distorted square-pyramidal (SP<sub>+</sub>) topology. The copper ion displacement from the basal planes toward the apical ligand is 0.2 Å. The most significant differences between the chloro and bromo structures are

observed in the Cu–X<sub>basal</sub> distances (average values are 2.276(5) and 2.434(3) Å for Cl and Br, respectively) and in the bridging angles (138.6(1) and 134.0(1)° for 2 and 3, respectively). This is in good accord with the smaller covalent radius for the chloride anion.

The most unusual feature of the crystal structures of compounds 2 and 3 is the occurrence of a polymeric zigzag chain structure as a result of the apical Cu–X bonding among the repeating units. The Cu(pepci) moieties are located on alternate sides of the chain presumably to minimize steric crowding. Steric requirements might also be responsible for the formation of the novel mono( $\mu$ -halide)-bridged chain structures. The pepci ligands are not exactly in alternate orientations on the stacking, one of the final pyridine groups being practically overlapped (Figure 4). The break in the parallelism between the consecutive pepci–X complexes causes a divergence of the two halide ligands, favoring the formation of only one halogen bridge, and giving rise to a zigzag chain.

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**Figure 3.** Enchainment along the [100] direction for [Cu(pepci)X]·(PF<sub>6</sub>) (X = Cl, Br) complexes.

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for [Cu(pepci)X]·(PF<sub>6</sub>) (X = Cl, Br)

	X = Cl	X = Br		X = Cl	X = Br
Cu1-X1	2.265(7)	2.434(3)	Cu3-X3	2.272(7)	2.382(3)
Cu1-N11	2.08(2)	2.01(1)	Cu3-N13	1.97(2)	1.95(1)
Cu1-N21	1.99(2)	2.00(1)	Cu3-N23	2.02(2)	2.02(2)
Cu1-N31	2.08(2)	2.00(2)	Cu3-N33	1.98(2)	2.03(1)
Cu1-X2	2.797(8)	2.856(3)	Cu3-X4	2.868(7)	2.871(6)
Cu2-X2	2.276(7)	2.400(3)	Cu4-X4	2.245(7)	2.419(3)
Cu2-N12	2.04(2)	1.95(2)	Cu4-N14	2.03(2)	2.06(1)
Cu2-N22	2.01(2)	2.02(1)	Cu4-N24	2.07(2)	1.94(1)
Cu2-N32	1.98(2)	1.97(1)	Cu4-N34	1.99(2)	1.92(2)
Cu2-X1	2.830(8)	2.866(3)	Cu4-X3	2.825(7)	2.888(3)
N21-Cu1-N31	171.8(8)	169.0(7)	N23-Cu3-N33	170.1(7)	170.2(6)
N11-Cu1-N31	81.6(8)	79.5(7)	N13-Cu3-N33	93.0(7)	94.5(7)
N11-Cu1-N21	90.4(8)	90.1(6)	N13-Cu3-N23	80.3(7)	77.4(7)
X1-Cu1-N31	92.2(6)	96.1(5)	X3-Cu3-N33	94.4(6)	94.6(4)
X1-Cu1-N21	95.9(6)	94.8(4)	X3-Cu3-N23	94.6(5)	95.0(5)
X1-Cu1-N11	157.0(5)	154.7(5)	X3-Cu3-N13	155.7(6)	154.7(5)
X1-Cu2-N32	84.7(6)	83.7(4)	X3-Cu4-N34	96.2(5)	94.7(5)
X1-Cu2-N22	90.3(5)	93.6(4)	X3-Cu4-N24	80.2(5)	83.5(4)
X1-Cu2-N12	102.2(5)	107.4(5)	X3-Cu4-N14	103.1(6)	107.9(4)
X1-Cu2-X2	98.5(2)	96.5(1)	X3-Cu4-X4	99.5(2)	96.6(1)
N22-Cu2-N32	172.0(8)	173.7(6)	N24-Cu4-N34	169.3(7)	170.9(7)
N12-Cu2-N32	82.5(7)	80.9(6)	N14-Cu4-N34	92.4(7)	93.3(7)
N12-Cu2-N22	92.5(7)	94.5(6)	N14-Cu4-N24	78.7(7)	78.8(6)
X2-Cu2-N32	93.3(6)	92.3(4)	X4-Cu4-N34	96.9(5)	94.8(5)
X2-Cu2-N22	93.6(5)	93.6(4)	X4-Cu4-N24	93.6(5)	94.3(4)
X2-Cu2-N12	158.3(5)	154.1(5)	X4-Cu4-N14	154.4(6)	153.4(5)
Cu1-X1-Cu2	138.3(3)	134.0(1)	Cu3-X3-Cu4	136.0(3)	134.9(1)
Cu1-X2-Cu2	137.6(3)	134.1(1)	Cu3-X4-Cu4	134.7(3)	134.9(1)

Mono( $\mu$ -chloro)-bridged copper(II) chain complexes are known;<sup>17</sup> however, mono( $\mu$ -bromo)-bridged chain structures are very scarce. The structural characteristics described so far for both compounds **2** and **3** are, as far as we are aware, absolutely unique in the literature. Preliminary results obtained for compound **3** were published recently.<sup>18</sup>

The Cu(1)–Cu(2) and Cu(3)–Cu(4) distances [4.766(5) and 4.730(4) Å for **2** and 4.846(4) and 4.851(4) Å for **3**] in the chain structures are considerably longer than those in a typical bis-( $\mu$ -bromo)-bridged structure like [Cu(py)Br<sub>2</sub>]<sub>2</sub> [3.643(9) Å]<sup>19</sup> but are comparable to Cu–Cu distances found in the mono( $\mu$ -chloro)-bridged copper(II) chain compounds.<sup>17</sup> The Cu–X–

Cu bridging angles are in the range of the Cu–Cl–Cu angles (114–145°) reported for such chain complexes.

**EPR Spectroscopy.** The X-band EPR spectra of polycrystalline samples of compounds **1–3** have been recorded at both room and liquid-nitrogen temperatures. The spectra are shown in Figure 5.

In the case of compounds **2** and **3** (Figure 5a), broad and isotropic signals appear in the EPR spectra, being narrower at low temperatures. The corresponding  $g_{\text{iso}}$  parameters have a value of 2.117 for both compounds. Absorptions due to the  $\Delta M_s = 2$  transition, of relative intensity, are also observed for these two complexes. This can probably be explained by the existence of two consecutive crystallographically independent copper(II) ions in the chain structures of the chloro and bromo compounds, having a dipole–dipole interaction. The distance ( $r$ ) between these Cu(II) ions has been calculated by the following expression: relative intensity = (intensity of  $\Delta M_s = 2$ /total intensity of  $\Delta M_s = 1$ ) =  $A r^{-6}(9.1/\nu^2)$  where  $\nu$  is the spectrometer operating frequency in GHz and  $A = 21 \pm 2$  is an experimental parameter.<sup>20</sup> The values thus obtained,  $r = 4.5$  and  $4.6$  Å for the chloro and bromo compounds, respectively, show a good agreement with those crystallographically determined [Cu···Cu ranging from 4.766(5) to 4.730(4) Å for **2** and from 4.846(4) to 4.881(4) Å for **3**].

The spectrum corresponding to the chloro compound (**1**) (Figure 5b) shows axial-type signals that remain practically unchanged from room temperature down to 100 K. The values obtained for the  $g$  tensor are  $g_{\parallel} = 2.219$ ,  $g_{\perp} = 2.059$ ,  $\langle g \rangle = 2.112$  and point toward a mainly copper(II)  $d_{x^2-y^2}$  orbital ground state. Likewise, a weak absorption corresponding to the  $\Delta M_s = 2$  forbidden transition can be observed at “half-field” values (164 mT). This signal is characteristic of the existence of interactions between two copper(II) ions to give a triplet state. An attempt to calculate the distance between these copper ions, from the relative intensities of both signals,<sup>20</sup> was not successful because of the partial overlapping of the mean signal with the  $\Delta M_s = 2$  one.

**Magnetic Properties.** The study of magnetic susceptibility data for the complexes has been performed within the temperature range 4.0–100K. The experimental data, plotted as the thermal variations of reciprocal susceptibility and the  $\chi_m T$  product, are shown in Figure 6 for hydrated chloro (**1**) and anhydrous chloro and bromo (**2** and **3**) compounds, respectively. The magnetic susceptibility data for compounds **2** and **3** are well described by the Curie–Weiss law above 10 K, with the values of  $\Theta \approx -1$  K and  $C = 0.40$  cm<sup>3</sup> K mol<sup>-1</sup> and  $\Theta \approx +0.5$  K and  $C = 0.40$  cm<sup>3</sup> K mol<sup>-1</sup> for **2** and **3**, respectively. The negative  $\Theta$  value and the overall appearance of the  $\chi_m T$  versus  $T$  curve (Figure 6) in the case of the chloro complex (**2**) are indicative of weak antiferromagnetic interactions between the Cu(II) centers. The data were analyzed using the Heisenberg model with exchange interaction between pairs of Cu(II) ions with spins  $S_i$  and  $S_j$  of the form

$$H = \sum_{i>j} H_{ij} = \sum_{i>j} -2J_{ij} S_i S_j$$

where we assumed interactions between nearest neighbor copper ions on a chain (i.e.,  $J_{ij} = J$  for  $j = i \pm 1$  and  $J_{ij} = 0$  otherwise).

The variation of magnetic susceptibility with temperature for this compound can satisfactorily be fitted to the empirical function introduced by Hall to represent the numerical calcula-

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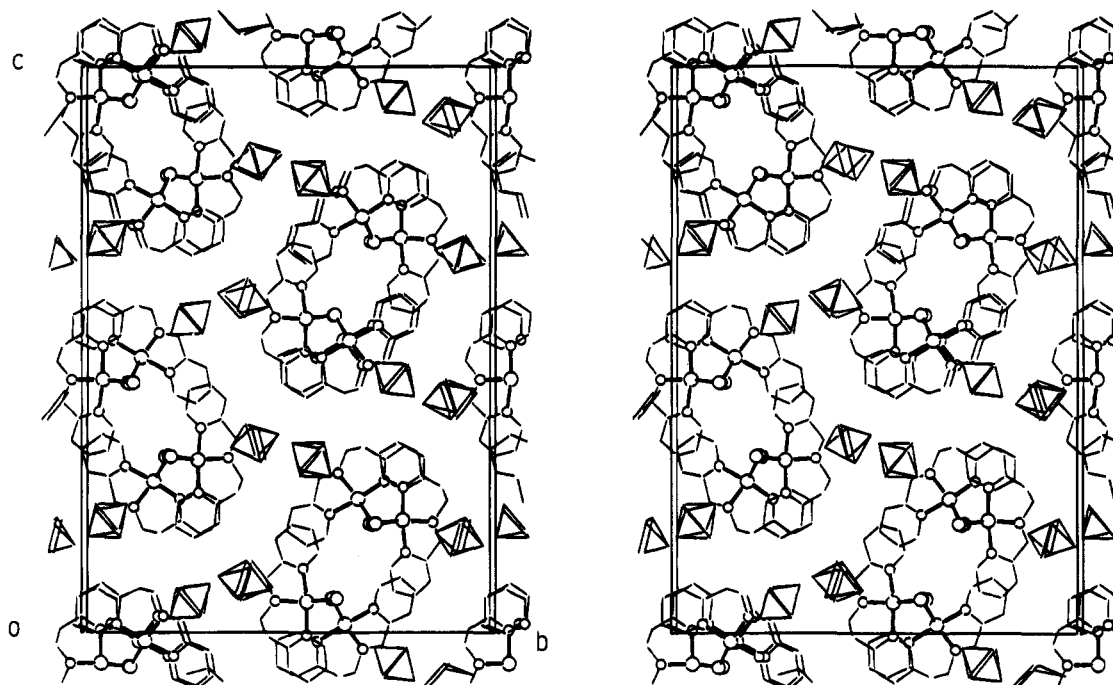


Figure 4. View of the chloride and bromide chain unit cells from the propagation direction.

tions performed by Bonner and Fisher describing a uniformly spaced chain of spins with  $S = 1/2$ :<sup>21</sup>

$$\chi = \frac{Ng^2\beta^2}{kT} \left[ \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \right]$$

where  $x = |J|/kT$ ,  $N$  and  $k$  are the Avogadro and Boltzmann constants,  $\beta$  is the Bohr magneton,  $A = 0.250$ ,  $B = 0.149\ 95$ ,  $C = 0.300\ 94$ ,  $D = 1.9862$ ,  $E = 0.688\ 54$ , and  $F = 6.0626$ . The resulting parameter was  $J/k = -2.0$  K ( $1.39$  cm<sup>-1</sup>) with  $g$  fixed at 2.117 from EPR measurements.

For the bromo chain **3** the increase in the  $\chi_m T$  value due to decreasing temperature is indicative of ferromagnetic type interactions in the compound. The variation of magnetic susceptibility with temperature for this compound could satisfactorily be fitted following the Baker et al. equation<sup>21</sup>

$$\chi = \frac{Ng^2\beta^2}{4kT} \left[ \frac{1 + Ax + Bx^2 + Cx^3 + Dx^4 + Ex^5}{1 + A'x + B'x^2 + C'x^3 + D'x^4} \right]^{2/3}$$

where  $x = |2J|/kT$  and

$$A = 5.797\ 991\ 6 \quad A' = 2.797\ 991\ 6$$

$$B = 16.902\ 653 \quad B' = 7.008\ 678\ 0$$

$$C = 29.376\ 885 \quad C' = 8.653\ 864\ 4$$

$$D = 29.832\ 959 \quad D' = 4.574\ 311\ 4$$

$$E = 14.036\ 918$$

The best fit to the ferromagnetic  $S \approx 1/2$  Heisenberg regular chain model was obtained for  $J/k = +1.0$  K ( $0.70$  cm<sup>-1</sup>) with  $g = 2.117$ . In both cases the interchain couplings were negligible.

The magnetic susceptibility of compound **1** follows a Curie–Weiss behavior for  $T > 25$  K, with a negative temperature intercept ( $\Theta$ ) of about  $-1$  K. The slope corresponds to a Curie constant of  $0.41$  cm<sup>3</sup> K mol<sup>-1</sup>. As the temperature is lowered, the product  $\chi_m T$ , proportional to the square of the effective magnetic moment, is practically constant ( $0.41$  cm<sup>3</sup> K mol<sup>-1</sup>) up to 25 K. This product decreases from  $0.41$  to  $0.24$  cm<sup>3</sup> K mol<sup>-1</sup> upon cooling down from 25 to 4 K. The variation observed is indicative of an antiferromagnetic coupling between Cu(II) ions. The susceptibility data were least-squares-fitted to the Bleaney–Bowers<sup>22</sup> equation for isotropic spin exchange in Cu<sup>II</sup> dimers ( $H = -2JS_1S_2$ )

$$\chi = \frac{Ng^2\beta^2}{kT} \left[ \frac{2}{3 + \exp\left(\frac{-2J}{kT}\right)} \right]$$

The best fit was obtained with the value  $J/k = -3$  K ( $2.09$  cm<sup>-1</sup>) and  $g$  fixed at 2.112 as obtained from EPR measurements.

**Magneto–Structural Trends.** Up to now, there have been only a few examples of both structural and magnetically characterized Cu<sup>II</sup> chain complexes containing mono( $\mu$ -halo) bridges<sup>17,23–25</sup> (see Table 5). As can be observed, only one Br-bridged chain of the type I is known in the literature.<sup>26</sup> The magnetic and structural parameters of compounds **2** and **3** are compiled and compared with those of related mono( $\mu$ -halo)-bridged compounds. The election of both  $\delta$  [angle X–Cu–L<sub>t</sub> (L<sub>t</sub> = ligand trans to X)] and  $\varphi$  [Cu–X–Cu bridging angle] angles (see structures **1** and **2**) to compare these complexes has been made on the basis of results of recent studies correlating bis( $\mu$ -halo)-bridged copper(II) dimers<sup>7,8</sup> and mono( $\mu$ -halo) cop-

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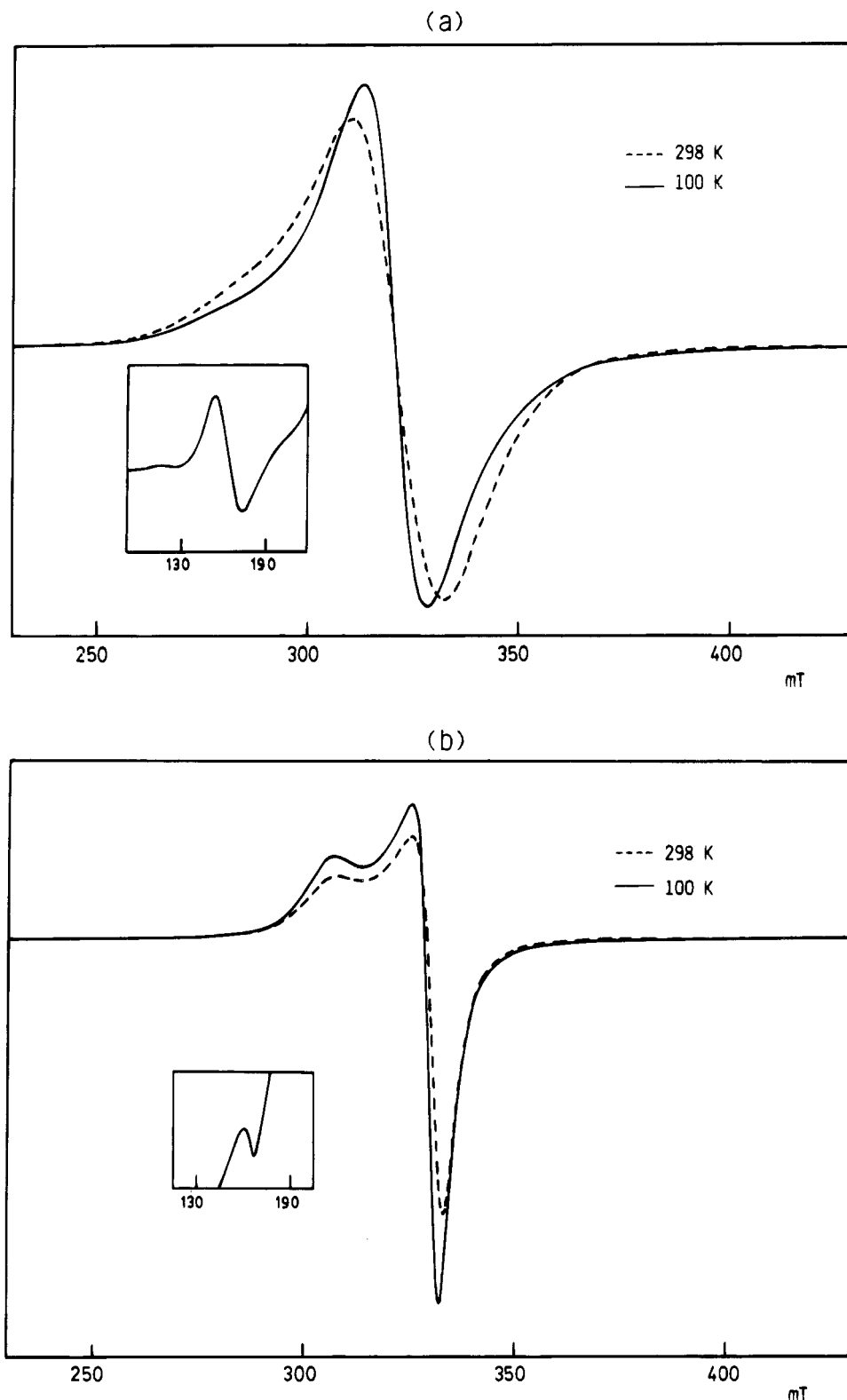
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**Figure 5.** X-band ESR spectra at room temperature (---) and at 100 K (—) for (a)  $[\text{Cu}(\text{pepci})\text{X}](\text{PF}_6)$  ( $\text{X} = \text{Cl}, \text{Br}$ ) (the spectra correspond to the bromo compound **3**) and (b)  $[\text{Cu}(\text{pepci})\text{Cl}](\text{PF}_6)\cdot\text{H}_2\text{O}$  (**1**).

per(II) chains.<sup>9</sup> These angles have been revealed as the more useful parameters to correlate with the exchange parameter  $J$  in these studies. The  $\delta$  angle gives an indication of the distortion of the coordination polyhedron of copper(II) with respect to the square-pyramidal and trigonal-bipyramidal geometries. As can be observed in Table 5, an increase in the distortion from the square-pyramidal to the trigonal-bipyramidal geometries (reflected by the  $\delta$  angle decreasing from 180 to 120°) produces stronger magnetic interactions. In the same way, an increase

in the value of the bridging angle from orthogonality ( $\varphi > 90^\circ$ ) favors the antiferromagnetic interactions.

From a theoretical point of view, extended Hückel molecular orbital (EHMO) calculations can be applied to the analysis of the exchange interactions for these kinds of systems. One-dimensional compounds with partially filled bands can behave in different ways.<sup>27–29</sup> In this sense, wide partially filled bands are associated with metallic behavior, whereas narrow ones correspond to the ferromagnetic and antiferromagnetic com-

Table 5. Geometrical and Magnetic Parameters for Cu(II) Chain Compounds of Type I<sup>a</sup>

compound	label <sup>b</sup>	repeat unit	$\delta$ , deg	$\varphi$ , deg	$J_{\text{exp}}$ , cm <sup>-1</sup>	$\Delta$ , meV	$J_{\text{calc}}$ , cm <sup>-1</sup>	ref
<i>trans</i> -[Cu(dmso)Cl <sub>2</sub> ]	a	O <sub>2</sub> Cl( $\mu$ -Cl)	146	145	-6.1	133	-3.99	17
[Cu(pepci)Cl]PF <sub>6</sub>	b	N <sub>3</sub> ( $\mu$ -Cl)	156	137	-1.39	70	-1.45	this work
[Cu(allH <sub>3</sub> )Cl <sub>3</sub> ]	c	NCl <sub>2</sub> ( $\mu$ -Cl)	154	112		12	-0.03	23
<i>cis</i> -[Cu(maep)Cl <sub>2</sub> ]	d	N <sub>2</sub> Cl( $\mu$ -Cl)	166	114	+1.58	2	0.00	24
<i>trans</i> -[Cu(ImH)Cl <sub>2</sub> ]	e	N <sub>2</sub> Cl( $\mu$ -Cl)	167	117	-2.1	7	-0.01	17
[Cu(paphy)Cl](PF <sub>6</sub> ) $\cdot$ H <sub>2</sub> O	f	N <sub>3</sub> ( $\mu$ -Cl)	168	102	+0.5	21	-0.10	25
<i>trans</i> -[Cu(caffeine)Cl <sub>2</sub> ]	g	NOCl( $\mu$ -Cl)	179	128	+0.48	0	0.00	17
<i>trans</i> -[Cu(dmso)Br <sub>2</sub> ]		O <sub>2</sub> Br( $\mu$ -Br)	146	145	-7.9	379	-33.3	26, 35
[Cu(pepci)Br]PF <sub>6</sub>		N <sub>3</sub> ( $\mu$ -Br)	154	134	+0.70	131	-4.21	this work

<sup>a</sup>  $\Delta$  and  $J_{\text{calc}}$  are the calculated gaps and coupling constants for modeled chains with structure I. dmso = dimethyl sulfoxide; pepci = *N*-(2-pyridylethyl)pyridine-2-carbaldimine; allH<sub>3</sub> = allopurinol; maep = 2-(2-(methylamino)ethyl)pyridine; ImH = imidazole; paphy = pyridine-2-carboxaldehyde 2'-pyridylhydrazone. <sup>b</sup> See Figure 7.

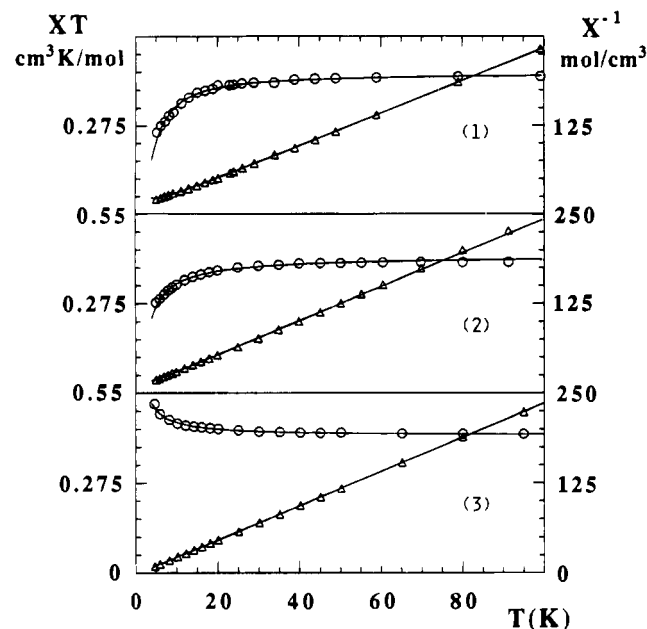


Figure 6. Thermal variation of the reciprocal susceptibility and  $\chi_m T$  for the anhydrous chloro (1) and hydrated chloro and bromo (2 and 3) compounds.

pounds.<sup>27</sup> EHMO calculations have been made for the title compounds on a modeled fragment,  $[\{\text{Cu}(\text{NH}_3)_3\text{Cl}\}]_n^{n+}$ , which generates the type I chains, by using the CACAO<sup>30</sup> program (atomic parameters were the internal of the program). The results are shown in Table 5 and Figure 7.

The global value of exchange interaction,  $J$ , corresponds to the sum of the ferro- and antiferromagnetic contributions.<sup>31,32</sup> The former is usually considered as approximately constant in series of analogous compounds. Antiferromagnetic interactions increase with the square of the bandwidth ( $\Delta^2$ ). For the systems with one unpaired electron per copper atom,  $J_{\text{AF}}$  can be given by the equation<sup>31,32</sup>

$$J_{\text{AF}} \approx \Delta^2/3\epsilon$$

where  $\Delta$  is the bandwidth and  $\epsilon$  is the mean energy of the

partially filled band. Therefore, the estimation of the geometry dependence of  $J_{\text{AF}}$  can be obtained by calculating  $\epsilon$  and  $\Delta$ , corresponding to the highest occupied band (HOB), at the extended Hückel level of these systems.

In the type I copper(II) chains, two limiting geometries exist for the five-coordinate copper environment. In a square-pyramidal coordination around the Cu(II) ion ( $\delta = 180^\circ$ ) the unpaired electron mainly resides in the  $d_{x^2-y^2}$  orbital, and a half-filled band formed by combination of such orbitals corresponds to the HOB. On the contrary, in a trigonal-bipyramidal environment ( $\delta = 120^\circ$ ) the electron resides in a  $d_{z^2}$  orbital, and the HOB must be the  $z^2$  band. The gradual change of the orbital  $x^2 - y^2$  to  $z^2$  when  $\delta$  changes from 180 to  $120^\circ$  has been previously described.<sup>33</sup> A study considering the variations of both  $\delta$  and  $\varphi$  angles was recently carried out.<sup>34</sup>

A representation of the theoretical bandwidths calculated for the modeled chain, as a function of  $\delta$  and  $\varphi$  angles (varying every  $5^\circ$ ), is shown in Figure 7a. As can be observed in this figure, distortion from square-pyramidal to trigonal-bipyramidal geometries ( $\delta$  angle decreasing from 180 to  $120^\circ$ ) and the increase of the bridging angle favor the antiferromagnetic interactions. The geometry of the halo-bridged unit for the reported compounds with the bridging halide atom occupying a basal position in the distorted square-pyramidal copper(II) and an axial position in the adjacent copper(II) environment determines a weak superexchange interaction due to the poor effective overlapping between the magnetic orbitals, essentially  $d_{x^2-y^2}$ , which are localized in the basal planes. As the distortion toward the trigonal bipyramid is increased, the magnetic orbitals become more strongly mixed with the  $d_{z^2}$  orbital and the magnetic interaction is stronger.<sup>35</sup>

In the same way, it can be observed in Figure 7a that the largest values of  $\Delta$  and therefore the stronger antiferromagnetic coupling occur for  $\delta \sim 120^\circ$  and  $\varphi \sim 150^\circ$ , whereas it is practically constant and small when  $\delta \sim 180^\circ$  and  $\varphi \sim 100^\circ$ . The predominant factor seems to be the value of the  $\delta$  angle. The trends reflected in this figure are in good qualitative accord with the experimental coupling constants shown in Table 5. The chloro complex 2 presents  $\delta$  and  $\varphi$  angles closer to 120 and  $150^\circ$ , respectively, and shows the second stronger exchange interaction constant. The variation of the bandwidth  $\Delta$  with the Cu-X apical distance has also been studied, and it can be observed in Figure 7b that the  $\Delta$  value decreases when the Cu-X distance is increasing.

With respect to the mono( $\mu$ -bromo) chains, only two compounds have been structurally and magnetically characterized.<sup>36</sup> From a theoretical point of view, the same tendency seems to

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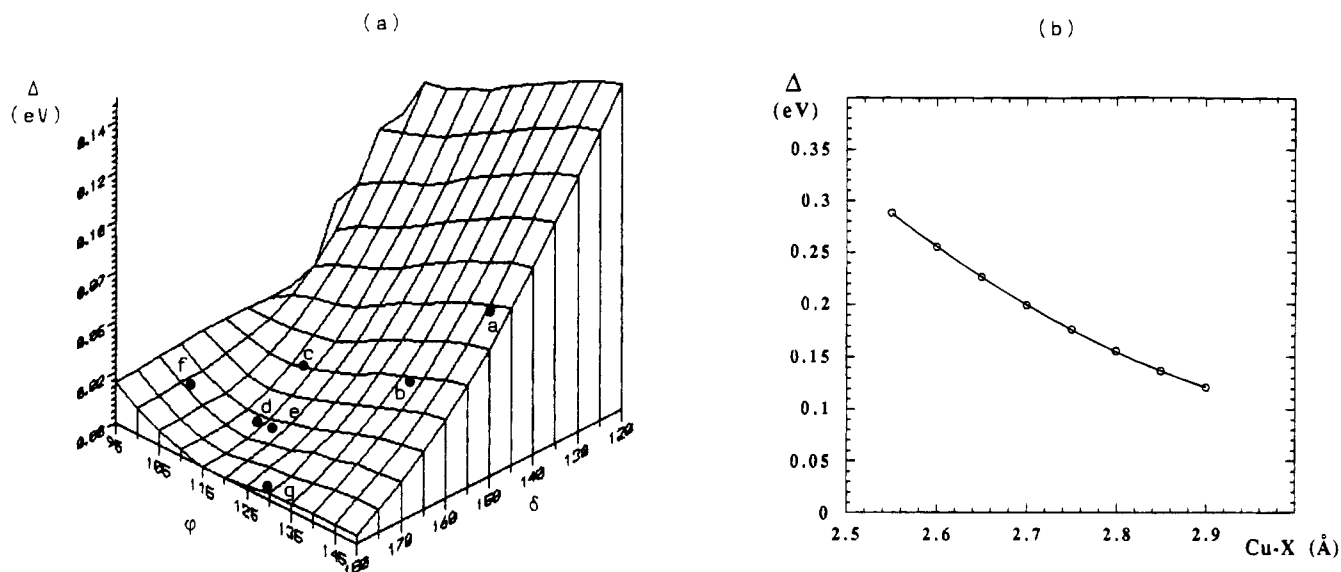
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**Figure 7.** (a) Representation of the gap ( $\Delta$ ) for the magnetic orbitals of the chloro chain compound (**2**) upon variation of the bridging ( $\varphi$ ) and torsion ( $\delta$ ) angles. (b) Variation of  $\Delta$  as a function of the apical Cu-Cl distance.

be exhibited by these types of chains (even with stronger antiferromagnetism). The experimental values of  $\delta$  and  $\varphi$  angles for compound **3** should then lead to a significant antiferromagnetic interaction. However, the interactions in this compound have shown to be ferromagnetic. More compounds of the type I with single bromine bridges would be desirable to establish magneto-structural correlations in this kind of compound.

### Concluding Remarks

Two unusual monohalide-bridged copper(II) chains were successfully obtained by following a developed synthetic strategy involving flexible tridentate aromatic amine ligands and noncoordinating counterions. In the case of the chloro complex, one hydrated compound was also obtained, postulated as a dimer.

As far as we are aware, the structural characteristics for both chloro and bromo copper(II) chains are absolutely unique in the literature. The pepci ligands are not exactly in alternate orientations on the stacking, one of the final pyridine groups being practically overlapped (Figure 4). This fact gives rise to an interaction consisting of a repulsive force applied on this part of the pepci ligand. The formation of the halogen bridge corresponds to an attractive force that draws the complexes toward each other. These contrary forces are not applied at the same point of the complex, the corresponding torque tending

to rotate it with an amplitude that depends on the relative intensity of each force. The angle of two successive complexes,  $44.1(3)^\circ$ , indicates a strong attraction due to the formation of the halide bridge. This break in the parallelism causes a divergence of the two halide ligands and favors the formation of only one halogen bridge, giving rise to a zigzag chain.

EPR measurements for chloro and bromo chains show the existence of significant dipolar interactions between pairs of copper(II) ions in both cases. Magneto-structural correlations have been analyzed by using extended Hückel MO calculations. At this point, it could be established that the main structural factor determining the strength of magnetic interactions is the  $\delta$  (N-Cu-X<sub>basal</sub>) angle with a maximum corresponding to the trigonal-bipyramidal topology ( $\delta = 120^\circ$ ). In the second place, the influence of the Cu-X apical distance must be considered. Weaker antiferromagnetic interactions have been observed when the apical distance has been large. Finally, the bridging angle  $\varphi$  has the minimum influence in the superexchange interaction.

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**Supplementary Material Available:** Tables giving crystal data and details of the structure determination, anisotropic thermal parameters, distortion of the coordination polyhedra, and complete bond distances and angles (20 pages). Ordering information is given on any current masthead page.

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