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Crystal structure and magnetic properties of the single- μ -chloro copper(II) chain [Cu(bipy)Cl₂] (bipy = 2,2'-bipyridine)

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Abstract

The crystal and molecular structure of the copper(II) chain [Cu(bipy)Cl₂] (1) (bipy = 2,2'-bipyridine) has been determined by X-ray diffraction methods. The crystal structure of 1 consists of neutral single chloro-bridged copper(II) chains with alternating short and long Cu–Cl distances through a screw axis parallel to *a*. The copper surrounding is best described as distorted square pyramidal, the equatorial plane being built by the two nitrogen atoms of the chelating bipy and two chlorine atoms (one terminal and the other bridging), whereas the apical position is filled by the bridging chlorine atom from the symmetry-related adjacent unit. The equatorial Cu–Cl bonds (2.291(3) and 2.259(3) Å) are shorter than the axial one (2.674(3) Å). The intrachain copper–copper separation is 4.010(3) Å whereas the shortest interchain copper–copper distance is 8.381(3) Å. The magnetic properties of 1 have been investigated in the temperature range 1.8–300 K. They reveal the occurrence of a weak intrachain antiferromagnetic coupling, J = -2.3 cm⁻¹ (uniformly-spaced linear chain of local spin S = 1/2). This value is compared to those of related mono- and di-chloro-bridged copper(II) polymers and the available magneto-structural data are discussed in the framework of a simple orbital model. (C) 1999 Elsevier Science S.A. All rights reserved.

Keywords: Copper complexes; Crystal structures; Bipyridine complexes; Chloro complexes; Magnetic properties

1. Introduction

A considerable amount of work has been carried out recently on the correlation of the structural and magnetic properties of monoatomic-bridged Cu(II) dimers. Qualitative and quantitative correlations between various structural features and magnetic behaviour have been postulated for the cases where the bridging atoms is a first-row atom [1-8]. In this context, a linear correlation has been found between J(isotropic electronic exchange parameter) and ϕ (angle at the hydroxo bridge) for the planar di-µ-hydroxo complexes $[CuL(OH)]_2^{n+}$, (L is a didentate ligand) [9–11]. It should be noted, however, that deviations from square-planar geometry at the metal or from planarity at the bridge lead to systems which violate this simple linear relationship between J and ϕ . The relatively simple concepts which have been successfully used for these cases, however, may not be directly applicable to systems bridged by second or third-row atoms, such as chloro- or bromo-bridged complexes [12–14]. The occurrence of relatively low-lying chloride or bromide d type orbitals which can interact with the metal orbitals accounts for that. A further complication

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in the complexes of the type $[CuLX_2]$ or $[CuA_2X_2]$ (where L and A are di- and monodentate ligands, respectively) is due to the wide variety of geometries that they can exhibit: coordination numbers of 4 (tetrahedral or square-planar), 5 (trigonal bipyramidal or square-pyramidal) or 6 (distorted octahedral), where the halogen atoms can act as terminal or bridging ligands occupying either axial and/or equatorial positions (in the plane and out-of-plane bridging modes) are observed, and discrete mono- or polynuclear complexes as well as chain compounds have been characterized (see Schemes 1–3). In this respect, a dichloro-bridged copper(II) chain (2) (see Scheme 2) with six-coordinated copper atom is obtained when $[Cu(bipy)Cl_2]$ (bipy is 2,2'-bipyridine) is recrystallized from dimethylacetamide [15]. However, its recrystallization from a water/ethanol solution leads to a monochloro-bridged copper(II) chain (1) (Scheme 3) with the same formula but with the copper atom being fivecoordinated, as shown thereunder. Consequently, the present

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I (di-µ-chloro dime

Scheme 1.







III (single-µ-chloro chain)

Scheme 3.

situation is that only a few examples for any given structural types are available precluding thus meaningful magnetostructural correlations to be made. This is one of the main reasons that justifies the continuous interest on this kind of systems. Here we report, the preparation, and the structural and magnetic characterization of a new phase (1, Scheme 3) of the compound of formula [Cu(bipy)Cl₂].

2. Experimental

2.1. Preparation of $[Cu(bipy)Cl_2]$ (1)

A mixture of $CuCl_2 \cdot 2H_2O$ (0.85 g, 5 mmol) and bipy (0.78 g, 5 mmol) was dissolved in a water/ethanol solution (20 ml). The resulting blue solution was filtered and allowed to stand at room temperature. Green crystals of formula $[Cu(bipy)Cl_2]$ (1) appeared after several months. They were hand picked and dried on filter paper. The crystal structure of 1 is presented here for the first time.

2.2. Physical techniques

The magnetic measurements were carried out on polycrystalline samples of **1** in the temperature range 1.8–300 K with a Quantum Design SQUID magnetometer operating at 100 G (low temperature region) and 1000 G (over all tem-

Table 1							
Crystal da	ata, da	ta collec	tion, stru	cture solut	ion and	refinement	for 1

•	
Chemical formula	$C_{10}H_8CuCl_2N_2$
Formula weight $(g \text{ mol}^{-1})$	290.62
Crystal system	monoclinic
Space group	I a
a (Å)	7.248(5)
b (Å)	17.862(5)
c (Å)	8.534(5)
β (°)	110.91(3)
$V(\text{\AA}^3)$	1032.1(10)
Ζ	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.870
F(000)	580.0
μ (Cu K α) (mm ⁻¹)	7.441
Data collection	
Radiation (Å)	Cu Ka, 1.54179
Monochromator	graphite
Temperature (K)	293(2)
θ Range (°)	2.12-58.93
Total data	806
Unique data	806
Observed data	806
No. reflections	791
No. refined parameters	137
$R(F^2)$	0.036
$wR(F^2)^a$	0.097
S ^b	1.083

^a $\omega = 1/[\sum (F_0^2)^2 + (0.08P)^2]; P = (F_0^2 + 2F_c^2)/3.$

^b $S = [\sum \omega (F_o^2 - F_c^2)/(m-n)]^{1/2}$, where *m* is the number of observed reflections and *n* is the number of parameters defined.

perature range). Diamagnetic corrections of the constituent atoms were estimated as -163×10^{-6} cm³ mol⁻¹ from Pascal's constants [17]. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism $(60 \times 10^{-6}$ cm³ mol⁻¹ per Cu(II)) and the magnetization of the sample holder.

2.3. X-ray crystallography of 1

A polyfacial prismatic crystal of approximate dimensions $0.52 \times 0.22 \times 0.11 \text{ mm}^3$ was put on a Stoe AED4 automatic four-circle diffractometer and used for data collec-Information concerning crystallographic tion. data collection and refinement of the structure is compiled in Table 1. Unit cell parameters and orientation matrix were determined from a least-squares treatment of the setting angles of 20 reflections with $5 < \theta < 15^{\circ}$ [18,19]. Examination of two standard reflections, monitored every hour, showed no sign of crystal deterioration. The index ranges of data collection were $0 \le h \le 8$, $0 \le k \le 19$ and $-9 \le l \le 8$. Data were corrected for Lorentz-polarization and absorption (cylindrical correction) [20]. The maximum and minimum transmission factors were 0.39 and 0.34.

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 , the computational programs used being the SIR92 [21] and SHELXL93 [22], respectively. All non-hydrogen atoms were refined anisotropically.

	,			
Copper environment				
Cu(1) - N(1)	2.037(8)		Cu(1)–N(2)	2.030(7)
Cu(1)–Cl(1)	2.291(3)		Cu(1)–Cl(2)	2.259(3)
$Cu(1)-Cl(1)^{i}$	2.674(3)		Cl(1)–Cu ⁱⁱ	2.674(3)
N(2)–Cu(1)–N(1)	79.6(3)		N(2)-Cu(1)-Cl(2)	171.5(2)
N(1)-Cu(1)-Cl(2)	93.6(2)		N(2)-Cu(1)-Cl(1)	92.3
N(1)-Cu(1)-Cl(1)	158.5(2)		Cl(2)-Cu(1)-Cl(1)	92.31(11)
$N(2)-Cu(1)-Cl(1)^{i}$	91.2(3)		$N(1)-Cu(1)-Cl(1)^{i}$	99.0(2)
$Cl(2)-Cu(1)-Cl(1)^{i}$	94.81(10)		$Cl(1)-Cu(1)-Cl(1)^{i}$	101.08(9)
$Cu(1)-Cl(1)-Cu(1)^{ii}$	107.50(10)			
$C-H\cdots Cl$ interactions				
D–H···A	D–H	$\mathbf{H} \cdot \cdot \cdot \mathbf{A}$	$D \cdots A$	$D – H \cdot \cdot \cdot A$
$C(1)-H(1)\cdots Cl(2)$	0.93(1)	2.629(10)	3.215(10)	121.6(10)
$C(10)-H(10)\cdots Cl(1)$	0.93(1)	2.686(9)	3.215(9)	116.8(10)
$C(9)-H(9)\cdots Cl(1)^{iii}$	0.93(1)	2.774(9)	3.616(9)	151.0(9)

Table 2 Selected bond distances (Å) and angles (°) for 1^a

^a Symmetry codes: (i) 1/2 + x, -y, z; (ii) x - 1/2, -y, z; (iii) 1 + x, y, 1 + z.

The hydrogen atoms from bipy were set in calculated positions and refined as riding atoms. They were included in the structure factor calculations with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the atom to which they are bonded. The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)2$ converged at *R* and R_w indices of 0.036 and 0.097. In the final difference map the residual maxima and minima were 0.419 and -0.445 e Å⁻³. The largest and mean Δ/σ are 0.003 and 0.001. The final geometrical calculations and the graphical manipulations were carried out with the PARST95 [23] and ORTEPII [24] programs, respectively. The selected bond lengths and distances for **1** are given in Table 2.

3. Results and discussion

3.1. Description of the structure of 1

The structure of complex 1 consists of neutral chains of $[Cu(bipy)Cl_2]$ units linked by single chloro bridges. The crystallographically independent monomeric unit is shown in Fig. 1 with the atom numbering scheme. A view of a segment of the uniform spaced chains growing through a screw axis parallel to *a* is depicted in Fig. 2 together with the interchain C–H···Cl contacts which link the chains through the *c* axis.

The coordination polyhedron around the copper atom can be described as distorted square pyramidal. The basal plane is built by two nitrogen atoms provided by the chelating bipy ligand and by two chlorine atoms, one being terminal and the other acting as bridge and occupying thus the apical position of the symmetry-related copper atom. The average Cu(1)–N bond length is 2.034(7) Å and the equatorial Cu(1)–Cl distances are unequal [2.291(2) and 2.259(3) Å for Cu(1)–Cl(1) and Cu(1)–Cl(2), respectively], but shorter



Fig. 1. Perspective view of crystallographically independent [Cu-(bipy)Cl₂] monomeric unit with the atom numbering. Thermal ellipsoids for the non-hydrogen atom are plotted at the 50% probability. Hydrogen atoms are given an arbitrary radius.

than the axial Cu(1)–Cl bond [2.674(3) Å for Cu(1)–Cl(1)ⁱ]. The bridging role of the Cl(1) atom accounts for the slight lengthening of the Cu(1)–Cl(1) bond distance when compared to that of the Cu(1)–Cl(2) bond. The copper atom is displaced by 0.20 Å from the mean N(1)N(2)Cl(1)Cl(2) basal plane towards the apical Cl(1)ⁱ atom. The angle at the bridging chlorine is 107.5(1)° and the intrachain copper-copper separation is 4.010(3) Å. The corresponding values in the related compound with the same formula but exhibiting a di-µ-chloro bridging pattern (**2**) are 89.57 and 99.62 ° and 3.802 and 3.876 Å [15].



Fig. 2. A view of the arrangement of compound 1 in the *ac* plane. The C-H···Cl contacts are illustrated by broken lines.

The value of the N···N 'bite' of bipy is 2.602(10) Å which falls in the normal range. Moreover, the angle subtended by bipy at the metal atom [79.6(3)° for N(1)–Cu(1)– N(2)] is close to those (80.6 and 81°) reported for bipy in other square pyramidal bipy-containing copper(II) complexes [25]. No unusual bond angles or bond lengths are observed for the coordinated bipy in the present compound. It is interesting to note that the five-membered chelated ring of bipy with copper assumes a *syn*-periplanar conformation. The dihedral angle between the two pyridine rings of bipy is $3.67(7)^\circ$. In the polymeric structure the bipy ligand form one set of parallel layers separated by a normal distance of 3.490(2) Å.

A series of intra- and inter-chain C–H···Cl contacts (see end of Table 2; broken lines in Fig. 2) holds together the neutral [Cu(bipy)Cl₂] units in the *ac* plane. The shortest interchain copper–copper separation is 8.381 Å.

3.2. Magnetic properties of 1

The magnetic behaviour of complex **1** is shown in Fig. 3 in the form of both $\chi_{\rm M}T$ and $\chi_{\rm M}$ plots versus $T(\chi_{\rm M}$ being the magnetic susceptibility per mol of copper atom). The value of $\chi_{\rm M}T$ at room temperature is 0.40 cm³ K mol⁻¹. This value decreases upon cooling and it vanishes at T = 0 K. The susceptibility attains a quasi constant value near 1.8 K most likely associated to the occurrence of a maximum in the very low temperature region. All these features are indicative of a weak intrachain antiferromagnetic coupling in 1.

From a structural point of view, **1** is a two-dimensional compound where the monochloro-bridged copper(II) chains are linked through hydrogen bonds involving the equatorial chlorine atom and the H(9)–C(9) bipy group. However, the exchange coupling through the C–H···Cl pathway is expected to be very weak and the magnetic coupling observed should be mainly mediated by bridging chlorine. Consequently, we can treat this compound as a monochloro-bridged copper(II) chain (uniformly-spaced linear chain of spin = 1/2) from a magnetic viewpoint. In order to analyze its magnetic behaviour, we have used the polynomial expression (1) developed by Hall [26] and which describes well the results of Bonner and Fisher [27] on uniformly-spaced linear chain of spin = 1/2.

$$\chi_{\rm M} = \frac{Ng^2\beta^2}{kT} \times \frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3} \quad (1)$$

where x = |J|/kT and the other parameters have their usual meanings. It is apparent from Fig. 3 that the value of *J* is very small and the applicability of Eq. (1) requires that $J \gg g\beta H$. Consequently, we used a low external magnetic field (H = 100 G) to ensure that the experimental data were field independent. The result of the fit through Eq. (1) (solid line in Fig. 3), leads to J = -2.3 cm⁻¹, g = 2.09 and R =



Fig. 3. $\chi_M T$ vs. *T* plot of compound **1** (the insert shows the thermal dependence of the magnetic susceptibility in the low temperature region): experimental (o) $\chi_M T$ and (Δ) χ_M data; best fit (—).

4.8×10⁻⁵. *R* is the agreement factor defined as $R = \sum [(\chi_M)_{obs} - (\chi_M)_{calc}]^2 / \sum [(\chi_M)_{obs}]^2$). The value of *J* is small as expected for this kind of compounds exhibiting the out-of-plane bridging framework. Keeping in mind that the magnetic orbital of the copper(II) in **1** is mainly delocalized in the equatorial plane and that a very weak spin density is expected on its axial position, a poor overlapping at the bridging chlorine can be anticipated and thus a weak antiferromagnetic coupling is predicted; (see Scheme 4).

The structures of a great variety of chloro-bridged copper(II) compounds have been determined aiming at correlating their structure and magnetic properties [12–14]. Selected magneto-structural data of the known out-of-plane di- μ -chloro-bridged copper(II) dimers and chains are summarized in Tables 3 and 4 whereas those concerning the monochloro-bridged copper(II) dimers are grouped in Table 5. It can be seen from these tables that there is no correlation between the value of *J* and the copper–copper separation. Consequently, a through-space mechanism for exchange coupling can be ruled out, and a more reasonable superexchange mechanism may be considered.

One can see that the magnetic coupling for all these outof-plane polynuclear compounds is relatively small (either ferro- or antiferromagnetic) because of the near orthogon-



Table 3
Structural and magnetic data of di-µ-chloro-bridged copper(II) dimers

Compound ^a	$J (\mathrm{cm}^{-1})$	ϕ^{b} (°)	$\alpha_b{}^c$	$\alpha_t{}^d$	R_0^{e} (Å)	$d_{\mathrm{Cu-Cu}}$ (Å)	Ref.
[Cu(tmso)Cl ₂] ₂	-16.0	88.5	145.7	165.2	3.02	3.74	[29]
[Cu(2-MePy)Cl ₂] ₂	-7.4	100.6	177.6	173.4	3.36	4.40	[30–32]
$[Cu(terpy)Cl]_2(PF_6)_2$	-5.8	89.9			2.72		[33]
$[Cu(tmen)Cl_2]_2$	-5.6	96.8	170.8	157.5	3.15	4.09	[34]
[Cu(Metz)(dmf)Cl ₂] ₂	-3.0	95.3			2.72		[12]
$[Cu(Me_2en)Cl_2]_2$	-2.2	86.1	167.7	173.6	2.73	3.46	[35]
$[Cu(Et_3en)Cl_2]_2$	+0.06	94.8	174.9	145.7	2.73	3.70	[36]
$[Cu(dmg)Cl_2]_2$	+6.3	88.0	166.7		2.70	3.44	[37–39]

^a Abbreviations used: tmso – tetramethylenesulfoxide, 2-MePy – 2-Methylpyridine, tmen – N,N,N',N'-tetramethylethylenediamine, Me₂en – N,N'-dimethylethylene diamine, dmg – dimethylglyoxime, terpy – N,N',N''-terpyridine, Et₃en — N,N,N'-triethylethylenediamine, mtz – 4-methylthiazole. ^b Value of the angle at the chloro bridge.

^c Value of the *trans* L-Cu-Cl(bridge) bond angle.

^d Value of the *trans* L–Cu–Cl(terminal) bond angle.

^e Axial copper to bridging chlorine bond distance.

Tixial copper to bridging emornic bond distance.

Table 4

Structural and magnetic data of di-µ-chloro-bridged copper(II) chains

Compound ^a	$J (\mathrm{cm}^{-1})$	ϕ^{b} (°)	$R_0^{\rm c}$ (Å)	$d_{\mathrm{Cu-Cu}}$ (Å)	Ref.
[Cu(bipy)Cl ₂]	-0.8	90.8	2.92	3.82	[15,16]
$[Cu(4-CNpy)_2Cl_2]_n$	-19.0	91.5	2.96	3.78	[40]
$[Cu(py)_2Cl_2]_n$	-18.4	88.5	3.03	3.85	[41-43]
$[Cu(4-vpy)_2Cl_2]_n$	-18.2	91.5	3.10	3.91	[44,45]
$[Cu(4-EtPy)_2Cl_2]_n$	-13.4	91.9	3.21	4.00	[45,46]
$[Cu(tz)_2Cl_2]_n$	-7.6	91.9	3.00	3.85	[47]
(Me ₃ NH)[CuCl ₃]·2H ₂ O	+1.2	93.4	2.83	3.90	[48–50]

^a Abbreviations used: bipy -2,2'-bipyridine, py - pyridine, 4-vpy -4-vinylpyridine, 4-EtPy -4-ethylpyridine, tz - thiazole, Me₃NH - trimethylammonium. ^b Value of the angle at the chloro bridge.

^c Axial copper to bridging chlorine bond distance.

Table 5 Structural and magnetic data of mono-µ-chloro-bridged copper(II) chains

$d_{\mathrm{Cu-Cu}}$ (Å)	Ref.
4.76	[51-53]
4.37	[53-55]
4.01	This work
4.60	[53,56]
4.26	[53,57]
	$ \frac{d_{Cu-Cu}(\text{\AA})}{4.76} \\ 4.37 \\ 4.01 \\ 4.60 \\ 4.26 $

^a Abbreviations used: dmso - dimethylsulfoxide, imH -imidazole, bipy - bipyridine, caf - caffeine, maep - 2-(2-methylaminoethyl)pyridine.

^b Value of the angle at the chloro bridge.

^c Value of the *trans* L–Cu–Cl(bridge) bond angle.

^d Value of the *trans* L-Cu-Cl(terminal) bond angle.

^e Axial copper to bridging chlorine bond distance.

ality of the magnetic orbitals as illustrated in Schemes 4 and 5. In this respect it should be noted that Ritter and Jansen's [28] calculations, using spherically symmetric Gaussian wave functions for the unperturbed atomic orbitals, predict reversal of the sign of *J* over a range of bridge angle between $80 < \phi < 120^{\circ}$. It can be seen in Tables 3–5 that the angle ϕ (angle at the chloro-bridge) is not the relevant parameter, as in the classical case represented by the di- μ -hydroxo copper(II) dimers. For the μ -chloro-bridged family, Hatfield [12] have considered the copper to bridging chlorine bond length (R_0) as an additional parameter and they observed a

rough dependence of *J* on the ϕ/R_0 quotient. Further refinements on the correct structural parameters will probably require that R_0 be raised to some power n or that an exponential expression $[\exp(-aR_0)]$ be adopted, as suggested by Marsh et al. [30]. It is very important to note that these chloro-bridged copper(II) compounds exhibit geometries comprised between square-pyramidal and trigonal bipyramidal. The values of *trans* L–Cu–L' angles can be used to follow this change in the copper geometry. These angles would be 180° for planar bases of the ideal square pyramid. The shorter this angle, the greater the deviation

from the square pyramidal geometry and the closer the trigonal bipyramid and therefore, an increase of spin density on the bridge is expected. In this sense, molecular orbital calculations by Hay et al. [8] on a hypothetical monochlorobridged copper(II) dimer have shown an increase of the antiferromagnetic coupling as the distortion proceeds from the square pyramidal geometry toward the trigonal bipyramidal one.

The values of the *trans* L–Cu–L' angle in the monochlorobridged copper(II) chains are included in Table 5. The pyramidal bases are not exactly planar, and the distortion from planarity increases in the order $Cu(maep)Cl_2 \approx Cu$ - $(imH)Cl_2 < Cu(caf)(H_2O)Cl_2 < Cu(bipy)Cl_2 < Cu(dmso)$ - Cl_2 , while the ϕ angle increases in the order $Cu(bipy)Cl_2 <$ $Cu(maep)Cl_2 < Cu(imH)Cl_2 < Cu(caf)(H_2O)Cl_2 < Cu(dmso)$ -Cl₂. In the light of these two trends, clearly the stronger antiferromagnetic coupling is predicted for the dmso-containing copper(II) complex, as observed. In the other cases, one can see that ϕ and α_{b} play against each other, and the magnetic coupling of the imidazole-containing compound and 1: they are very close because the effect of the smaller ϕ angle for 1 is counterbalanced by its greater degree of distortion ($\alpha_{\rm b}$). These observations are also valid in the case of the di-µ-chloro-bridged copper(II) dimers listed in Table 3. For the corresponding di-µ-chloro-bridged copper(II) chains (Table 4) the values of the α_b and α_t bond angles are not important because they are practically constant and very close to 180° .

Finally, a comparison between the values of J from Table 5 and those from Tables 3 and 4 reveals that in general the di-µ-chloro families exhibit a larger coupling than the single-µ-chloro one in spite of the smaller value of ϕ for the former. This can be easily understood in the context of the simple orbital model proposed by Kahn et al. [58-60]. The magnetic coupling in this model is proportional to the square of the overlapping integral at the bridge (see Schemes 4 and 5). So, the value of J for the di- μ -chlorobridged copper(II) compounds should be roughly four times that of the single-chloro-bridged ones everything being equal. The smaller value of the angle at the bridging atom for the di-µ-chloro bridged family and the different distortions of the metal surrounding account for the deviations from this prediction. In this respect it deserves to be outlined that the compound [Cu(bpy)Cl₂] crystallizes in two different phases: uniform mono-µ-chloro-bridged (present work) and alternating di-µ-chloro-bridged [15,16] copper(II) chains a function of the solvent used in the synthetic process. This is quite curious because the solvent is not involved in the crystal structures. The magnetic properties of this last compound were analyzed through an alternating chain model and the resulting values of J and α were -0.83 and 0.22 cm⁻¹, respectively [16] (where $\alpha = 0$ corresponds to the dimer case and $\alpha = 1$ corresponds to the uniform chain). In spite of the di-µ-chloro-bridge nature of this compound, the electronic exchange parameter has a smaller value than that of compound 1. Again, the smaller value of the ϕ angle in the alternating chain accounts for this decrease of J.

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