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Notes

Synthesis and Structural Characterization of the One-Dimensional $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$ Complex (3-Clpy = 3-Chloropyridine): A Singular Ferrimagnetic Chain with Local $S_A = S_B$

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Introduction

One-dimensional ferrimagnetism is synonymous of antiferromagnetic coupling between alternated spins $S_A \neq S_B$, which allows a net magnetic moment. Some examples of $\{Mn\ Cu\}_n$ or $\{Mn\ Ni\}_n$ have been reported in recent years[1] together with some examples of mixed coordination compound−radical units.[2] When the same scheme is applied to 3-D compounds, ferrimagnetism becomes a useful tool to obtain molecular based magnets such as the prussian blue-like compounds, in which S_A and S_B were obtained from heterometallic systems or mixed-valence homometallic paramagnetic centers.[3] To try to obtain ferrimagnetic chains from homometallic systems with $S_A = S_B$ is a priori an inappropriate strategy, but ferrimagnetism may be obtained from the adequate topology of the chain: it is necessary to find ferromagnetic coupling alternated with two consecutive antiferromagnetic interactions, Figure 1. In the present work we report the synthesis and structural characterization of the one-dimensional compound $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$, in which 3-Clpy is 3-chloropyridine. Magnetic measurements indicate that, in agreement with the structural data, the chain shows a regular alternancy of two ferromagnetic and two antiferromagnetic interactions, with global ferrimagnetic behavior.

An additional interest of the title compound lies in the large value of 129.1(3)° found for one of the Cu−N−Cu bond angles of one of the end-on azide bridges present in the compound, which is involved in an overall antiferromagnetic pathway (see Chart 1). The double end-on bridge or the end-on azido bridge together with another monatomic bridge such as hydroxo or phenoxo have a characteristic Cu−N−Cu bond angle[4] around 100°, but the recent contributions of Thompson et al. point out that one end-on azido bridge and a second diatomic bridge as pyridazine[5] allow for greater Cu−N−Cu bond angles, typically in the 110−115° range.

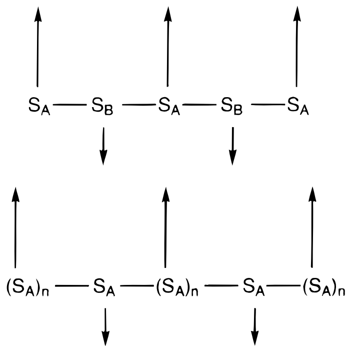

Figure 1. (a) Classical ferrimagnetic chain scheme from antiferromagnetic interactions between S_A and S_B alternated spins. (b) Topological ferrimagnetic chain from a ferro−antiferromagnetic interaction for S_A local spins.

Similar bond angles have recently been obtained in end-on azide/carboxylate simultaneous bridges.[6] From these results, antiferromagnetic coupling has been proposed for end-on azido bridges with Cu−N−Cu bond angles greater than 108°.[5] In our case the second bridge is a triatomic ligand and the greatest Cu−N−Cu bond angle reported to date has been obtained (129.1°), and in agreement with the Thompson proposal, it should contribute to the antiferromagnetic coupling in the mixed 1,1 and 1,3 bridge.

Experimental Section

Caution. *Azide derivatives are potentially explosive! Only a small amount of material should be prepared, and it should be handled with caution.*

Preparation of $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$. An aqueous solution of sodium azide (0.195 g, 3 mmol) was added to a mixture of copper(II) nitrate trihydrate (0.72 g, 3 mmol) and 3-chloropyridine (1.13 g, 10 mmol) in 40 mL of acetone. The solution was filtered, and the filtrate was allowed to stand in a refrigerator for 3−4 weeks to grow well-formed black crystals of the $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$ complex. Anal. Calcd for $C_{10}Cl_2CuH_8N_8$: C, 32.05; H, 2.16; N, 29.91; Cu, 16.96. Found: C, 31.9; H, 2.2; N, 30.0; Cu, 16.7.

Crystallographic Data Collection and Refinement of the Structure. The X-ray single-crystal data were collected on a modified STOE four-circle diffractometer. Crystal size: 0.80 × 0.30 × 0.25 mm. The crystallographic data, conditions retained for the intensity data collec-

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Chart 1

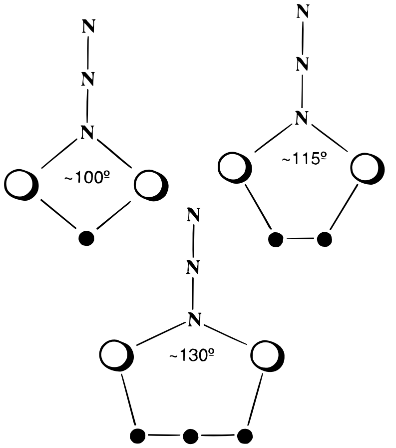

Table 1. Crystallographic Data for $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$

chem. formula	$C_{10}H_8Cl_2Cu\,N_8$
a, Å	15.113(7)
b, Å	13.483(6)
c, Å	15.801(9)
β, deg	116.93(4)
V, Å^3	2871(3)
Z	8
fw	374.68
space group	$P2_1/c$
T, K	293(2)
λ(Mo Kα), Å	0.716 09
d_{calc}, g·cm^{-3}	1.734
μ(Mo Kα), mm^{-1}	1.899
R^a	0.0572
$R^2\omega^b$	0.1282

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R\omega(F_o)^2 = \{\sum[\omega\,(F_o)^2 - (F_c)^2)^2]/\sum[\omega(F_o)^4]\}^{1/2}$.

tion, and some features of the structure refinements are listed in Table 1. Graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) with the ω-scan technique was used to collect the data. The accurate unit cell parameters were determined from automatic centering of 30 reflections ($8° < \theta < 11°$) and refined by least-squares methods. A total of 4670 reflections (3897 independent reflections, $R_{int} = 0.0438$) were collected in the range $3.38° < \theta < 23.50°$. The intensities of two control reflections ($\bar{4}14$; $\bar{4}02$), measured every 50 min, dropped continuously during data collection by 25%. Corrections were applied for Lorentz–polarization effects, intensity decay, and absorption[7] (range of normalized transmission coefficients: 0.338–1.000). The structure was solved by direct methods using the SHELXS-86 computer program[8] and refined by full-matrix least-squares methods on F^2, using the SHELXL-93 computer program[9] incorporated in SHELXTL/PC V 5.03 program package.[10] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on calculated positions and assigned with isotropic displacement parameters (4 common, 1 for each 3-Clpy molecule). The final R indices are 0.0572 ($R1$) and 0.1282 (w$R2$) [$I > 2\sigma(I)$]. The number of refined parameters was 386. Goodness-of-fit: 1.026. Maximum and minimum peaks in the final difference Fourier synthesis were 0.425 and −0.563 e Å^{-3}. Final atomic coordinates are reported in Table 2 and significant bond parameters are given in Table 3.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 x 10^3) for $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$

atom	x	y	z	U(eq)
Cu(1)	0	0	0	30(1)
Cu(2)	2456(1)	−67(1)	354(1)	33(1)
Cu(3)	5000	0	0	38(1)
N(11)	653(4)	−229(4)	−841(4)	36(1)
N(12)	233(4)	−455(5)	−1622(5)	55(2)
N(13)	−190(6)	−664(9)	−2408(7)	164(5)
N(21)	3159(4)	−268(4)	−440(4)	36(1)
N(22)	2668(4)	−412(4)	−1260(5)	46(2)
N(23)	2237(5)	−520(7)	−2080(5)	87(3)
N(31)	1767(4)	184(4)	1154(4)	37(1)
N(32)	2170(4)	245(4)	1985(4)	34(1)
N(33)	2520(5)	293(6)	2789(5)	85(3)
N(41)	5311(4)	480(4)	1295(4)	42(2)
N(42)	4758(4)	303(4)	1623(4)	35(1)
N(43)	4218(4)	148(4)	1954(4)	54(2)
N(1)	−30(4)	1484(4)	−261(4)	34(1)
C(1)	495(5)	2124(5)	435(5)	38(2)
C(2)	528(5)	3122(5)	288(6)	44(2)
Cl(1)	1251(2)	3875(1)	1228(2)	72(1)
C(3)	−13(6)	3489(6)	−622(6)	57(2)
C(4)	−562(6)	2845(6)	−1329(6)	55(2)
C(5)	−556(5)	1856(5)	−1139(5)	41(2)
N(2)	2466(4)	1416(4)	64(4)	35(1)
C(6)	3096(5)	2042(5)	698(5)	38(2)
C(7)	3171(5)	3015(5)	487(5)	43(2)
Cl(2)	4023(2)	3780(2)	1340(2)	72(1)
C(8)	2588(5)	3381(5)	−418(5)	47(2)
C(9)	1926(5)	2729(5)	−1077(5)	49(2)
C(10)	1885(5)	1751(5)	−829(5)	42(2)
N(3)	2575(4)	−1545(4)	659(4)	35(1)
C(11)	2085(5)	−2194(5)	−32(5)	42(2)
C(12)	2117(5)	−3210(5)	136(6)	49(2)
Cl(3)	1417(2)	−3976(2)	−813(2)	76(1)
C(13)	2683(6)	−3578(6)	1025(7)	59(2)
C(14)	3188(6)	−2909(6)	1711(6)	65(2)
C(15)	3129(5)	−1893(5)	1532(5)	49(2)
N(4)	4791(4)	1422(4)	−461(4)	37(1)
C(16)	5392(5)	2136(5)	96(5)	41(2)
C(17)	5296(5)	3109(5)	−181(6)	46(2)
Cl(4)	6101(2)	3966(1)	599(2)	68(1)
C(18)	4573(6)	3375(6)	−1058(6)	55(2)
C(19)	3950(6)	2648(6)	−1619(6)	58(2)
C(20)	4097(5)	1692(5)	−1300(5)	48(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

Description of the Structure. An ORTEP plot of the basic unit of $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$ is shown in Figure 2. The structure consists of neutral chains of copper atoms linked by azido bridges. Coordination around the copper atoms consists of N-atoms from 3-chloropyridine ligands in trans and four azido bridges, two of which are placed on the axis of an elongated octahedron. Three kinds of copper atom are present in the structure: Cu(1) shows two double end-on azido bridges with Cu(2) and Cu(2A) with Cu(1)–N(11)–Cu(2) and Cu(1)–N(31)–Cu(2) bond angles of 100.3(2) and 102.4(2)°, respectively. Bond distances show a short Cu(1)–N(11) length of 2.006(5) Å and a large Cu(1)–N(31) distance of 2.471(5) Å. Cu(2) shows the two end-on bridges with Cu(1) and two azido bridges with Cu(3), one of them end-on and the other end-to-end. Bond distances are the short Cu(2)–N(21) 1.997(5) Å and the long Cu(2)–N(43) 2.733(6) Å. The uncommon Cu(2)–N(21)–Cu(3) bond angle of 129.1(3)° is due to the large Cu(2)···Cu(3) distance of 4.130(2) Å forced by the end-to-end azido bridge. Finally, Cu(3) shows two double mixed bridges end-to-end and end-on with Cu(2) and Cu(2B) with a Cu(3)–

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$

Cu(1)···Cu(2)	3.495(2)	Cu(2)···Cu(3)	4.130(2)		
Cu(1)−N(1)	2.040(5)	Cu(2)−N(3)	2.040(5)	Cu(3)−N(41)	1.988(5)
Cu(1)−N(11)	2.006(5)	Cu(2)−N(11)	2.525(5)	Cu(3)−N(4)	2.025(5)
Cu(1)−N(31)	2.471(5)	Cu(2)−N(31)	1.997(5)	Cu(3)−N(21)	2.569(5)
		Cu(2)−N(21)	1.997(5)		
		Cu(2)−N(2)	2.053(5)		
		Cu(2)−N(43)	2.733(6)		
N(11)−N(12)	1.144(7)	N(31)−N(32)	1.173(7)		
N(12)−N(13)	1.146(9)	N(32)−N(33)	1.136(8)		
N(21)−N(22)	1.182(8)	N(41)−N(42)	1.190(7)		
N(22)−N(23)	1.166(9)	N(42)−N(43)	1.171(8)		
N(11)−N(12)-N(13)	178.8(11)	N(31)−N(32)-N(33)	176.9(7)		
N(21)−N(22)-N(23)	175.0(8)	N(41)−N(42)-N(43)	178.6(6)		
Cu(1)···Cu(2)···Cu(3)	164.60(3)	N(11)−Cu(2)-N(31)	78.1(2)		
Cu(1)−N(11)-Cu(2)	100.3(2)	N(43)−Cu(2)-N(21)	91.3(2)		
Cu(1)−N(31)-Cu(2)	102.4(2)	N(41)−Cu(3)-N(21)	92.7(2)		
Cu(2)−N(21)-Cu(3)	129.1(3)	Cu(2)−N(43)-N(42)	101.0(5)		
N(11)−Cu(1)-N(31)	79.2(2)	N(42)−N(41)-Cu(3)	119.8(4)		

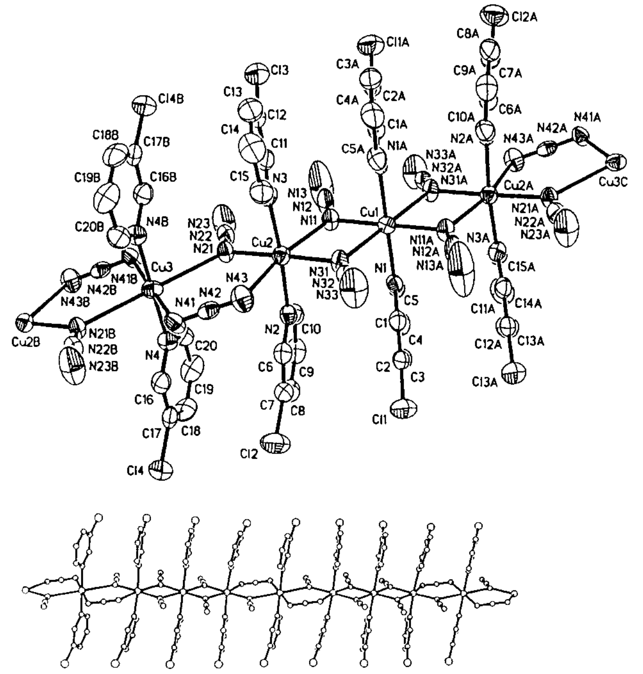

Figure 2. ORTEP drawing (50% of thermal ellipsoid probability) of $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$ with atom-labeling scheme.

N(21) 2.569(5) Å long distance and a Cu(3)−N(41) 1.988(5) Å short distance. The chain may be described as the alternance of two groups of the mixed end-to-end and end-on bridges with two groups of double end-on bridges along the one-dimensional compound.

Magnetic Properties. Plot of the $\chi_M T$ product vs T in the temperature range of 300−2 K is shown in Figure 3. The minimum $\chi_M T$ value of 0.989 $cm^3 \cdot K \cdot mol^{-1}$ at 10 K, placed between the room temperature and the 2 K values of 1.360 and 1.722 $cm^{-3} \cdot K \cdot mol^{-1}$, respectively, corresponds to the typical shape of a ferrimagnetic system. If one takes into account that $S_A = S_B$, the only possibility to explain this behavior is by means of two different J_1 and J_2 coupling constants for the two kinds of bridge present along the chain, with a $J_1J_1-J_2J_2$ alternance, and with the assumption that the two J values have opposite signs, which is to say the interactions should be one ferromagnetic and the second antiferromagnetic.

Analytical expressions for a system with two J_1 alternated with two J_2 interactions are not available, and a fit of the experimental data was performed in numerical form from a full-matrix diagonalization[11] of the Hamiltonian corresponding to a ring of 12 local $S = {}^1/_2$ centers with the adequate alternance of J_1J_1 and J_2J_2. The best fit parameters obtained by minimizing the R factor $= (\sum \chi_M T^{calc} - \chi_M T^{obs})^2/(\chi_M T^{obs})^2$, where $J_1 = -19.6$ cm^{-1}, $J_2 = +10.6$ cm^{-1}, $g = 2.21$, and $R = 4.3 \times 10^{-4}$. The fit shows a small deviation only in the very low-temperature range despite the ground state for the ferrimagnetic 12 coppers ring being the limiting value $S = 3$.

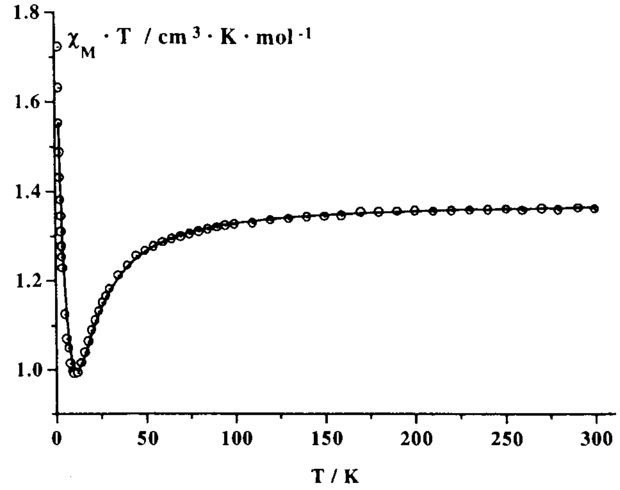

Figure 3. $\chi_M T$ vs T plot for $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$. The solid line shows the best fit theoretical curve obtained from full-matrix diagonalization of the Hamiltonian corresponding to a 12-copper ring (see text).

From the topology of the chain, which shows three parallel and one antiparallel spins for each Cu_4 unit, the molar magnetization measurement at 2 K confirms the ferrimagnetic behavior of the chain: the plot of $M/N\beta$ vs applied magnetic field reach a 1.9 value in 2S units and tends to the $S = 1$ for each of four cooper atoms, Figure 4. EPR spectra show the typical shape of an axial copper(II) with $g_{\parallel} = 2.22$ and $g_{\perp} = 2.05$, as may be expected from structural data.

This topologic ferrimagnetic behavior with $S_A = S_B$ suggests a new way to build ferrimagnetic compounds from ferromagnetic building blocks linked by means of antiferromagnetic interactions, independently of the local spin values.

The J_2 value of $+10.6$ cm^{-1} may be unambiguously assigned to the $Cu(\mu_{1,1}\text{-}N_3)_2Cu$ bridges, which typically show ferromag-

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(11) CLUMAG program: Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231.

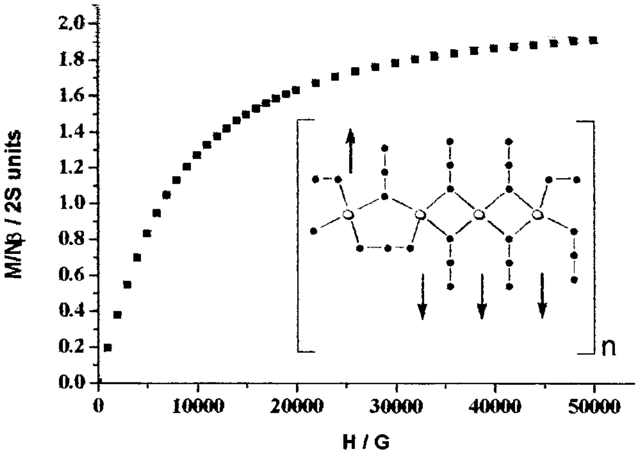

Figure 4. Molar magnetization measurement for $[Cu(3\text{-}Clpy)_2(N_3)_2]_n$ assuming the $n = 4$ sequence as molar unit. As corresponds to the spin arrangement, a final $S = 1$ spin is reached at high field.

netic interactions for bond angles close to 100°.[12] The J_1 value of -19.6 cm^{-1} should be assigned to the Cu($\mu_{1,1}$-N$_3$)($\mu_{1,3}$-N$_3$)-Cu unit, which show two different superexchange pathways. This J_1 value is similar to or greater than the values found for two end-to-end bridges,[13] such as $(\mu_{1,3}\text{-}N_3)_2[Cu(pmdn)]_2(BPh_4)_2$ (-13 cm^{-1}) and greater than the expected coupling for an interaction through one ferromagnetic and one an antiferromagnetic pathway. On the basis of this result, antiferromagnetic contribution to the superexchange may be proposed for the end-on bridge in this case, due to the very large value of the Cu−N−Cu bond angle of 129.1° and an overall antiferromagnetic coupling for the Cu(2)−Cu(3) interaction.

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Supporting Information Available: Complete listings of full data collection and processing parameters, bond lengths and bond angles, atomic coordinates, equivalent isotropic and anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients (10 pages). Ordering information is given on any current masthead page.

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