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Metal-Biradical Chains from a High-Spin Ligand and Bis(hexafluoroacetylacetonato)copper(II)

Chandrasekar Rajadurai,[†,‡] Volker Enkelmann,[†] Vladimir Ikorskii,[||] Victor I. Ovcharenko,*[,||] and Martin Baumgarten*[,†]

Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany,
International Tomography Center, Siberian Branch of the Russian Academy of Sciences, 630090,
Novosibirsk, Russia, and Institute of Nanotechnology, Research Center Karlsruhe, Postfach-3640,
D- 76021, Germany

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The synthesis, X-ray crystal structure, and magnetic studies of a rare example of organic/inorganic spin hybrid clusters extended in infinite ladder-type chain $[Cu(C_5F_6HO_2)_2]_7(C_{35}H_{35}N_5O_4)_2$ ([**Cu(hfac)**$_2$]$_7$(**pyacbisNN**)$_2$, **2**) formed by the reaction of a high spin nitronylnitroxide biradical $C_{35}H_{35}N_5O_4$ (**pyacbisNN**, **1**) and bis(hexafluroacetylacetonate)-copper(II) = **Cu(hfac)$_2$** are described. Single-crystal X-ray structure analysis revealed the triclinic $P\bar{1}$ space group of **2** with the following parameters: a =10.6191(4) Å, b = 19.6384(7) Å, c = 21.941(9) Å, α = 107.111(7)°, β = 95.107(8)°, γ = 94.208(0)°, Z = 2. Each repeating unit in **2** carries a centrosymmetric cyclic six spin and a linear five spin cluster with four different copper coordination environments having octahedral and square planar geometries. These clusters are interconnected to form infinite chains which are running along the crystallographic b axis. The magnetic measurements show nearly paramagnetic behavior with very small variations over a large temperature range. The magnetic properties are thus result of complex competitions of many weak ferro- and antiferromagnetic interactions, which appear as small deviations from quite linear μ_{eff} vs T dependence at low temperature. At high temperature (300–14 K), antiferromagnetic behavior dominates a little, while at very low temperature (14–2 K), a small increase of μ_{eff} was observed. The magnetic susceptibility data are described by the Curie–Weiss law [$\chi = C/(T - \theta)$] with the optimal parameters $C = 4.32 \pm 0.01$ emuK/mol and $\theta = -0.6 \pm 0.3$ K, where C is the Curie constant and θ is the Weiss temperature.

Introduction

The combination of different organic radicals and paramagnetic metal ions ("metal-radical approach") to form new heterospin hybrid systems is a well-known strategy.[1−20] It has been pointed out earlier by Gatteschi and Rey that stable radicals such as nitronylnitroxides (NN) and iminonitroxides (IN) themselves, already offer two coordination sites for metal complexation yielding a variety of different type of structures.[1a−e] Thus, it turned out to be intriguing, further testing functionalized high-spin ground-state biradicals containing NN as bridging units between metal(hfac)$_2$ in order to increase the dimensionality of the complexes or clusters. However, only scarce reports are available on this topic. The Cambridge Crystallographic Database showed only eight metal NN radical structures where biradicals were used as

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* To whom correspondence should be addressed. E-mail: martin.baumgarten@mpip-mainz.mpg.de (M.B.); Victor.Ovcharenko@tomo.nsc.ru (V.O.). Phone: +49-6131-379248 (M.B.); +7-3832-33-1222 (V.O.). Fax: +49-6131-379370 (M.B.); +7-3832-33-1399 (V.O.).

[†] Max Planck Institute for Polymer Research.

[‡] Institute of Nanotechnology.

[||] International Tomography Center.

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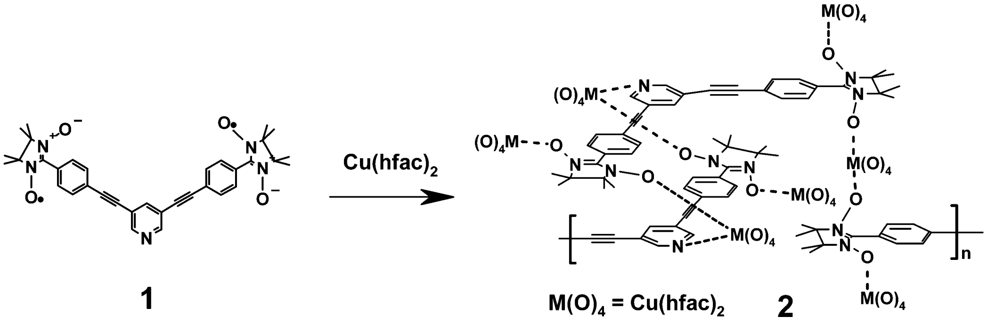
Chart 1. Reaction of **1** with Cu(hfac)$_2$



ligands (partly low-spin ground states) so far, and only one of them extended into higher dimensions.[21] The structural novelty of a high-spin ligand upon reaction with paramagnetic metal centers can yield interesting and unusual regiospecific magnetic exchange interaction pathways.

Hence we report herein such an example of a ladder type chain of clusters **2** [**Cu(hfac)**$_2$]$_7$(**pyacbisNN**)$_2$ carrying cyclic and linear spin cluster systems in a single chain formed by the reaction of pentadentate NN-based high-spin biradical **1**,[22] with **Cu(hfac)**$_2$ (Chart 1). The synthesis, structural novelty, and magnetic properties of **2** will be discussed.

Experimental Section

Cu(hfac)$_2$ dihydrate was purchased from Aldrich and used as received. Dichloromethane and hexane solvents were used as received. **PyacbisNN 1** was synthesized as described in our previously published procedure.[22]

Synthesis of 2. Biradical **1** (5.5 mg, 0.009 mmol) and 31.0 mg (0.060 mmol) of Cu(hfac)$_2$ dihydrate were dissolved in dichloromethane, and hexane was diffused slowly into it. The formed microcrystals were isolated. These crystals were again recrystallized in a dichloromethane/hexane mixture (1:2) for 2 days to afford 8.7 mg of blue-green-colored crystals of **2** (21%). The composition of **2** was determined by X-ray crystallography. Temperature dependent static magnetic susceptibilities of the randomly oriented single-crystalline sample was recorded using MPMS-5S (Quantum Design) SQUID magnetometer over a temperature range of 2−300 K in a homogeneous external dc magnetic field of up to 5 kOe. The magnetic field dependence of molar magnetic susceptibility, χ, was not found. The diamagnetic corrections of the molar magnetic susceptibilities were applied using well-known Pascal's constants. The effective magnetic moment was calculated by the formula $\mu_{\mathrm{eff}} = [(3k/N_A\beta^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$, where k is Boltzmann's constant, N_A is the Avogadro number, and β is the Bohr magneton.

X-ray data collection was performed on a Nonius KCCD diffractometer with graphite-monochromated Mo Kα radiation at 120 K. The structures were solved by direct methods (CRYSTALS). Refinement was done with anisotropic temperature factors for all non-hydrogen atoms. The H atoms were refined with fixed isotropic temperature factors in the riding mode. The crystals used for diffraction study showed no decomposition during data collections.

Result and Discussion

X-ray Structure. X-ray structure analysis revealed the triclinic $P\bar{1}$ symmetry of **2**, where all the potential five coordination sites of ligand **1** are occupied by the Cu(hfac)$_2$. The ORTEP drawing of the molecular structure of the titled complex **2** is shown in Figure 1a. Each repeat unit is comprised of two molecules of **2** in centrosymmetric dimeric form carrying seven Cu(hfac)$_2$ molecules, which extend as ladder chain along the crystallographic *b* axis. In total, there are four different copper environments in each repeating unit [two octahedral (Oh) and two square pyramidal (SP) geometries] with different Cu−O and Cu−N bond lengths. Both Cu(2) and Cu(4) have coordination number six, and Cu(1) and Cu(3) possess 5-fold coordination. A clear view of the all the four coppers' coordination environments is presented in Figure 2. In one octahedral copper complex, pyridyl nitrogen N(3) from **1**, one NN oxygen O(11) from another molecule of **1**, and four hfac oxygens together form a Cu(2) centered octahedral [MO$_5$N$_1$-type] geometry. The radical oxygen (O11) and the pyridine nitrogen (N3) are cis-coordinated to copper Cu(2) with a N(3)−Cu(2)-O(11) bond angle of 96.5° (see Table 2). One oxygen O(11) from the NN and the other oxygen O(72) from hfac are in the *z* axis of the octahedron and N(3) bound to the Cu(2) in the *x*−*y* plane with the Cu(2)−N(3) distance of 1.998 Å. The lone

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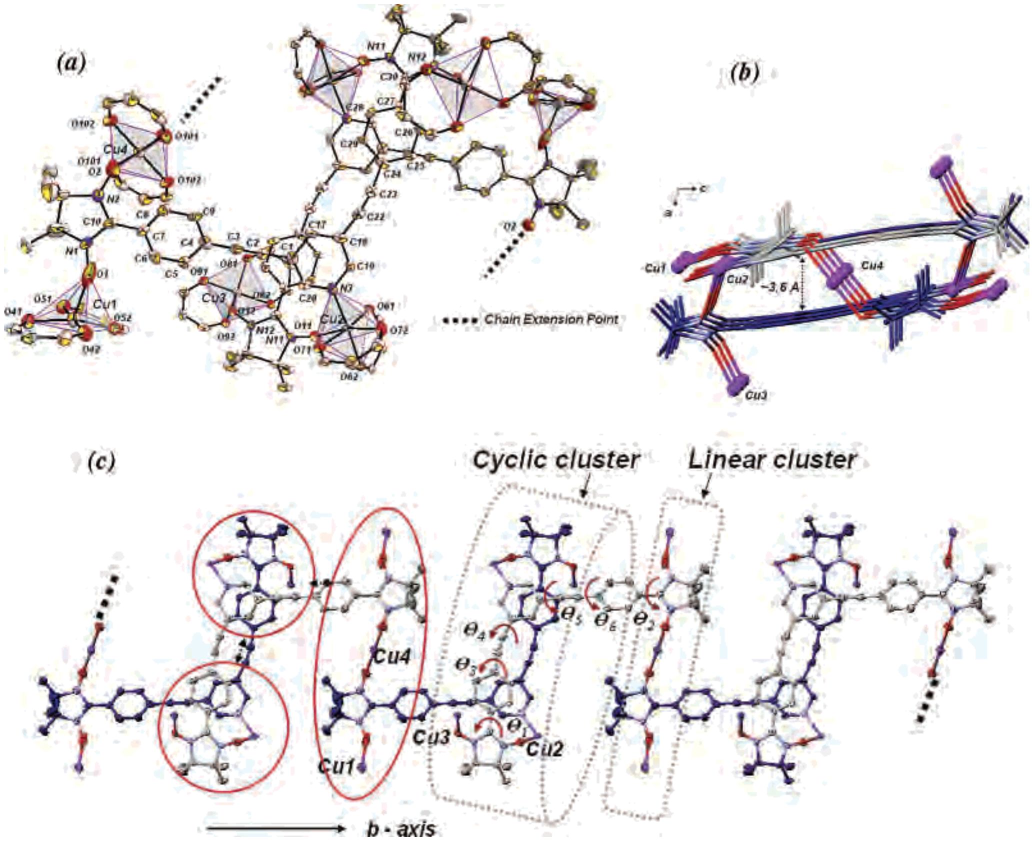

Figure 1. (a) ORTEP (50% probability ellipsoids) view of a segment of one chain in **2** with the atom numbering used in the main text. Hydrogen atoms and CF_3 groups are omitted for clarity. (b) View along the chain running *b* axis. (c) Ball and stick representation of the chain running along the crystallographic *b* axis. The gray color dotted cylindrical and broken rectangular lines show the cyclic and linear clusters, respectively. The red circles and black double-headed arrows show the trimeric and pentameric motifs and their interaction. The dihedral angles are $\theta_1 = 21.5°$; $\theta_2 = 23.7°$; $\theta_3 = 3.2°$; $\theta_4 = 5.5°$; $\theta_5 = 22.9°$; and $\theta_6 = 22.9°$.

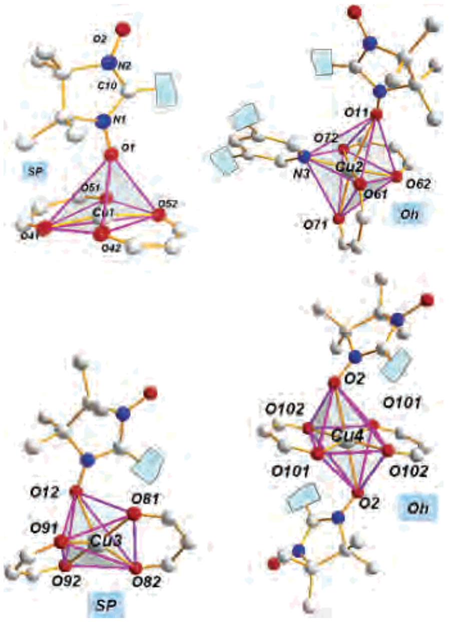

Figure 2. Ball and stick representation of the four types of copper coordination environments present in the complex **2**. In the figure, hydrogen atoms and CF_3 groups are omitted for clarity. Labels Oh and SP stand for octahedral and square pyramidal, respectively.

pair of electrons on the pyridyl nitrogen is linearly directed to the Cu as suggested by the Cu(2)−N(3)−C(17) angle of 179°.

Table 1. Crystallographic Parameters for **2**

	2
empirical formula	$C_{70}H_{42}Cu_{3.5}F_{42}O_{18}N_5$
temp, K	120
wavelength (Mo Kα), Å	0.71073
crystal system, space group	triclinic, $P\bar{1}$
a, Å	10.6191(4)
b, Å	19.6384(7)
c, Å	21.9418(8)
α (°)	107.1117(14)
β (°)	95.1078(12)
γ (°)	94.2080(12)
V (Å^3)	4331.93
Z, ρ_{cald} (g/cm^3)	2, 1.734
abs coeff (cm^{-1})	1.007
F (000)	2244.595
cryst size (mm^3)	0.38 × 0.22 × 0.09
θ range for data collection (°)	0−27.5
index ranges	$13 \le h \le 13$
	$25 \le k \le 24$
	$0 \le l \le 28$
reflns collected/unique	40 178/19 121
refinement method	full-matrix least-squares on *F*
data/restraints/params	7876/0/1189
GOF on F^2	1.174
final *R* indices [$I > 2\sigma(I)$]	$R = 0.0719$, $R_w = 0.0490$

The Cu(4) connects the two NN oxygens O(2) of the two molecules of **1**, forming a tetragonally distorted Oh complex with 6-fold oxygen coordination [MO_6-type]. Here, the oxygens from the two NN units are trans-coordinated to the Cu(4) [O(2)−Cu(4)−O(2) bond angle: 180°], forming the

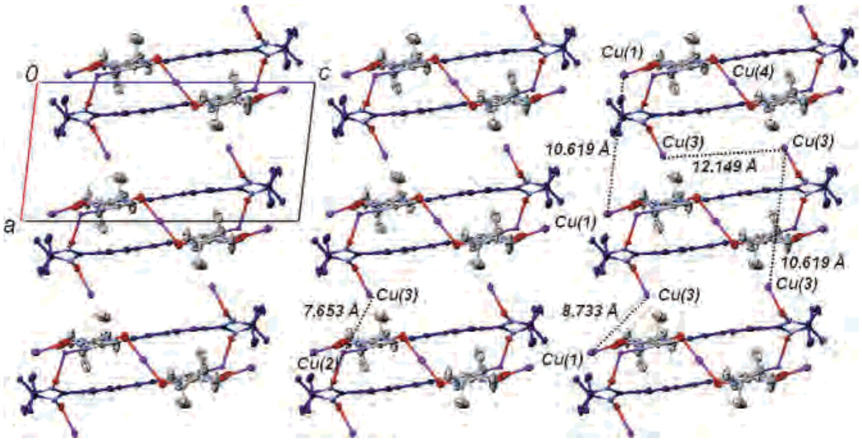

Figure 3. Chain packing view of complex **2** along the crystallographic *a*−*c* plane; in the figure, hydrogen atoms and CF_3 groups are omitted for clarity. The labels show the interchain Cu−Cu distances.

Table 2. Selected Structural Parameters for **2**

	Cu(1)	Cu(2)	Cu(3)	Cu(4)
geometry	square pyramidal	octahedral	square pyramidal	octahedral
MX_n -type	CuO_5	CuO_5N_1	CuO_5	CuO_6
NO−Cu coord mode	axial	axial	axial	axial
pyridine−Cu coord mode		equatorial		
NO−Cu−ON				trans
NO−Cu−pyridine		cis		
bond lengths (Å)	Cu(1)−O(1), 2.147(0) Cu(1)−O(41), 1.891(5) Cu(1)−O(42), 1.934(4) Cu(1)−O(51), 1.947(7) Cu(1)−O(52), 1.895(0)	Cu(2)−O(11), 2.491(5) Cu(2)−N(3), 1.998(3) Cu(2)−O(61), 1.958(4) Cu(2)−O(62), 1.965(7) Cu(2)−O(71), 1.946(6) Cu(2)−O(72), 2.204(4)	Cu(3)−O(12), 2.254(3) Cu(3)−O(81), 1.957(1) Cu(3)−O(82), 1.935(6) Cu(3)−O(91), 1.910(4) Cu(3)−O(92), 1.966(4)	Cu(4)−O(2), 2.359(3) Cu(4)−O(101), 1.945(2) Cu(4)−O(102), 1.952(6)
bond angles Cu−O−N	150.76°	141.26°	121.20°	125.15°
other bond angles (deg)	N(1)−O(1)−Cu(1), 150.75(9)	N(3)−Cu(2)−O(11), 96.48(4)	N(12)−O(12)−Cu(3), 121.20(2)	O(2)−Cu(4)−O(2), 180.00(0)
		N(11)−O(11)−Cu(2), 141.26(5) C(17)−N(3)−Cu(2), 178.67		N(2)−O(2)−Cu(4), 125.15(1)

z axis of the distorted octahedron with the total O−O distance of 4.72 Å and the remaining hfac oxygens occupy the *x*−*y* plane. In the square pyramidal coppers, the two Cu(1) and Cu(3) centers have five coordination sites, where solely one NN oxygen and four hfac oxygens are involved in building the square pyramidal [MO_5-type] geometries. Importantly, both Cu(2) and Cu(4) play unique role by bridging the two biradicals **1**, forming cyclic and linear spin systems along the crystallographic chain propagating *b* axis. Interestingly, in the cyclic spin system, the aryl ethynyl bond is slightly bent with an angle of ca. 171° to form the cyclic ring with the C≡C bond distance of C(22)−C(23) 1.20 Å. In the linear spin system, the phenyl ethynyl and pyridyl ethynyl connectivity are almost linear with the angles 179.2° and 176.2°, respectively, with the C≡C bond distance of C(2)−C(3) 1.19 Å. It is important to notice here that in all four different copper environments the NN radical units are axially bound to the copper and all of the N−O group π^* orbital is nearly orthogonal to the coppers ($d_{x^2-y^2}$) magnetic orbitals. The overlap angle of the radical oxygen (Cu−O−N) with the different copper ions is decreasing in the following order, Cu(1) = 150.8° > Cu(2) = 141.3° > Cu(4) = 125.2° > Cu(3) > 121.2°. The distance between the radical oxygen and the copper(II) ion is decreasing in the following order, Cu(2)−O(11) = 2.49 Å > Cu(4)−O(2) = 2.36 Å > Cu(3)−O(12) = 2.25 Å > Cu(1)−O(1) = 2.15 Å. The shortest interchain Cu−Cu distance is 7.65 Å (Figure 3).

Magneto-Structural Correlations. The results of the magnetic measurements are presented in Figure 4. The magnetic susceptibility data are described by the Curie−Weiss law [$\chi = C/(T - \theta)$] with optimal parameters $C = 4.32 \pm 0.01$ emu K/mol and $\theta = -0.6 \pm 0.3$ K. Based on the Curie constant *C*, the calculated effective magnetic

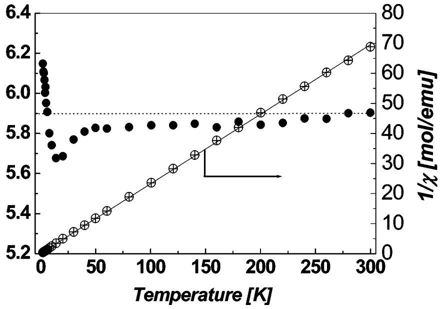

Figure 4. Temperature dependence of the reciprocal magnetic susceptibility (right ordinate axis; solid line presents theoretical curve with optimal parameters) and the effective magnetic moment (left ordinate axis) for **2** measured at an applied DC field of 5 kOe.

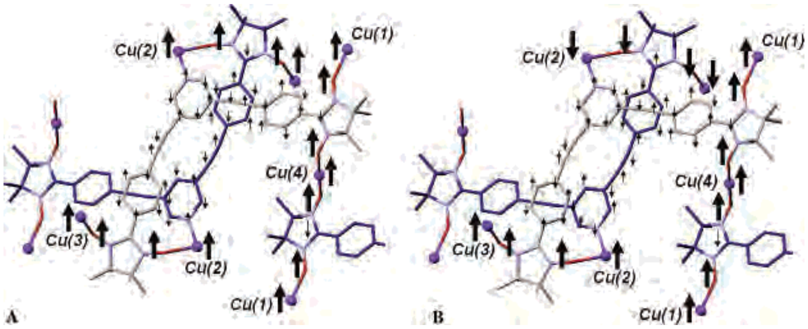

Figure 5. Qualitative spin polarization pathways for the intratrimer (A or B) and trimer−linear pentamer ferromagnetic interactions.

moment is equal to 5.88 μ_B (where μ_B is the Bohr magneton). This value exactly corresponds to the system of weakly coupled seven Cu(II) ions ($g = 2.07$) and four nitroxide fragments from **2** biradicals ($g = 2.00$). The μ_{eff} value is 5.88 μ_B at 300 K, which slightly decreased and reached a minimum of 5.68 μ_B at 14 K, below 14 K, the value steeply increased to 6.15 μ_B at 2 K. From the magneto-structural point of view one can visualize two types of clusters in a chain, (i) a "*cyclic* six spin system" shaped by the coordination of two NN units and two pyridine nitrogens from two different biradicals with Cu(2) and Cu(3) concurrently carrying a total of $^6/_2$ spins in a cycle, where Cu(3) is extracyclic, and (ii) a "*linear five spin system*" formed by the arrangement of Cu(1)−NN−Cu(4)−NN−Cu(1) having a total of $^5/_2$ spins with an axial overlap of the radical oxygen (pπ) with the copper's d_{z^2} orbital (see Figure 2). Additionally, in both Cu(3) and Cu(2), the radical oxygen is bound to the copper axially leading to possible ferromagnetic (FM) interaction. In the cyclic six-spin system, the dihedral angle between the planes of the phenyl ring and the NN five-member ring is $\theta_1 = 21.5°$, and in the linear six-spin system, the dihedral angle between the phenyl ring plane and the NN five member ring plane is $\theta_2 = 23.7°$. On the basis of four different copper types, we can expect four major exchange coupling constants (J) between the radical units and the copper ions. Unfortunately, the complex nature of the structure makes it difficult to extract any meaningful exchange coupling constants. However comparison with known Cu-radical complexes offers some guide to analyze the magneto-structural relationship in the present system.[1]

In the high-temperature range of 300−14 K, as shown in Figure 4a nearly paramagnetic behavior is found; however, one would expect ferromagnetic behavior considering the four types of copper where the radical N−O is axially bound to the copper ion.[1a] The X-ray analysis showed no structural change from 120 to 300 K, thus ruling out the possibility of any geometrical deformation (axial to equatorial conversion) in this temperature range. The magnetic behavior can be described by assuming weak interactions through a phenylethynyl spacer,[22] and one can observe two trimeric spin systems [Cu(3)−NN−Cu(2)] in the cyclic six spin system and a pentameric spin system in each repeating unit separated by arylethynyl spacers (Figure 1c). The exchange interaction within each cluster cannot be weak due to the close proximity of metal and radical spins but could still have different signs for the different Cu−ON geometries, where it is known that at short distances (here Cu(1)−O(1) = 2.15 Å) antiferromagnetic exchange could be provided.[13] The magnetic properties are thus a result of complex competitions of many weak ferro- and antiferromagnetic interactions, which appear as small deviations from quite linear μ_{eff} vs T dependence at low temperature. For the biradical itself, it has earlier been found that only below 15 K an enhanced triplet occupation occurs.[22] Thus, the small increase of μ_{eff} below 14 K could be in agreement with an increase in triplet nature.

The possible spin polarization pathways[23] are depicted in Figure 5a,b. The spin polarization through the biradical unit connecting a trimeric cluster and the linear five-spin unit should be ferromagnetic, but effective only at low temperatures. The interaction between the two trimers through the pyridyl spacer in the center, equatorially bound to Cu(2) with the Cu(2)−N(3) distance of 2.00 Å could be positive or negative (Figure 5a vs b).

However, at temperatures below 15 K the small raise of μ_{eff} value down to 2 K seems very well in accord with the enhanced triplet occupation of the biradical unit leading to effective ferromagnetic exchange interaction between the cyclic trimeric and the linear pentameric spin system. It can, however, not be ruled out that the minimum at 14 K with increase below, is connected also with a small change in structure at this very low temperature (e.g., axial to equatorial conversion). An abrupt increase at low temperatures was found for the biradical chain described earlier,[21] assumed to be combined with a phase transition. Although we cannot fully exclude at this even lower temperature there is no tendency toward sudden variation of our μ_{eff} dependence. The observed smooth and very small change in magnetization observed here in contrast to ref 21, however, is more in line with the former explained exchange through the spacer, with further triplet occupation at low temperatures.

Conclusion

In conclusion, compound **2** is one of the rare examples of a structurally novel *heterospin* compound having two types of clusters with four different types of coppers in chains where a high-spin biradical acts as a bridging ligand. Furthermore, the above approximated analysis highlights the importance of considering unexpected and complex regiospecific interactions due to the structural novelty. Further

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work on exploiting the ligand **2** with other metalhexafluoroacetylacetonates (M = Mn^{2+}, Co^{2+}) is underway.

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Supporting Information Available: Crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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