

Ferromagnetic Interactions in Heterobimetallic Chains Formed through the Secondary Coordination of Dithiolene Complexes

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A novel paramagnetic ($S = 1/2$) copper dithiolene complex based on the tfadt ligand (tfadt: 3-trifluoromethylacrylonitrile-2,3-dithiolate) is prepared as its $n\text{-Bu}_4\text{N}^+$ salt and crystallized with $[\text{Ni}(\text{cyclam})]^{2+}$ into infinite, one-dimensional chains through $\text{CN} \cdots \text{Ni}$ interactions, avoiding any direct (antiferromagnetic) overlap between the dithiolene complexes. An unprecedented ferromagnetic interaction within the heterobimetallic chains between the $S = 1/2$ $[\text{Cu}(\text{tfadt})_2]^{2-}$ and the $S = 1$ $[\text{Ni}(\text{cyclam})]^{2+}$ tectons is observed, despite the fact that the SOMOs of both $[\text{Cu}(\text{tfadt})_2]^{2-}$ (with $d_{x^2-y^2}$ symmetry) and $[\text{Ni}(\text{cyclam})]^{2+}$ (with $d_{x^2-y^2}$ and d_z symmetry) have the same e_g symmetry. The experimental exchange interaction deduced from the fit of the magnetic susceptibility ($J_{\text{exp}}/k_B = +5.0$ K) was confirmed by theoretical calculations ($J_{\text{cal}}/k_B = +7.3$ K), and a rationale is given for the presence of an intrachain ferromagnetic interaction.

Introduction

Dithiolene complexes offer a wide variety of applications, in material science in their radical forms as in bioinorganic chemistry as enzyme models.^{1,2} This is due to the noninnocent character of the 1,2-dithiolate ligand which gives the complexes the ability to exist in several stable oxidation states,³ some of them being paramagnetic. As a consequence of their open-shell character, these complexes have been extensively involved in the elaboration of magnetic and/or conducting materials.^{4,5} In most situations, however, *antiferromagnetic* interactions through direct $\pi \cdots \pi$ overlap between the radical species were recurrently observed. Strong *antiferromagnetic* interactions developing in stacks or layers give rise to partially filled conduction

bands and associated metallic conductivity⁶ while weak *antiferromagnetic* interactions allows for the formation of 3D *antiferromagnets*,⁷ spin ladders,^{8,9} or spin chains, eventually affected by spin-Peierls¹⁰ or abrupt paramagnetic–diamagnetic transitions.^{11,12} Very few systems were reported to exhibit *ferromagnetic* interactions, and bulk ferromagnetism is limited to two examples, $[\text{NH}_4][\text{Ni}(\text{mnt})_2]$ based on uniform stacks¹³ and $[\text{Cp}^*_2\text{Mn}][\text{Ni}(\text{dmit})_2]$ built from alternated stacks.¹⁴

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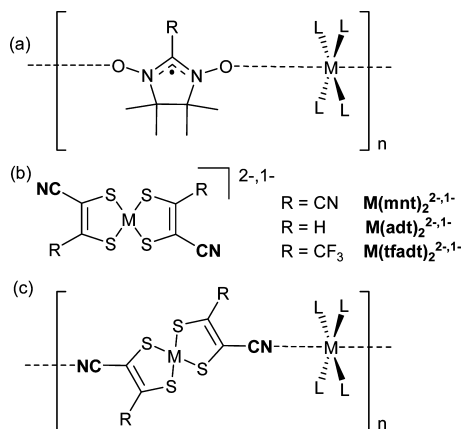
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Chart 1



Indeed, magnetic chain systems have attracted attention for many years,¹⁵ and the discovery of bimetallic chain compounds¹⁶ or polymeric transition metal complexes with nitronylnitroxide bridging ligands¹⁷ opened new concepts in the field such as 1D-ferrimagnetism. This was also recently followed by the strong interest raised by single-chain magnets (SCM)^{18,19} where ferro- or ferrimagnetic spin configurations within the chains are associated with a large anisotropy. In this context, paramagnetic dithiolene complexes were only very recently investigated as *bridging coordinating* centers between transition metal complexes, in the same way nitronylnitroxides do through $\text{N}-\text{O} \cdots \text{M} \text{L}_n \cdots$ interactions (Chart 1a).

Indeed, it was shown that the nitrile moieties of paramagnetic complexes such as $\text{Ni}(\text{mnt})_2^-$, $\text{Ni}(\text{adt})_2^-$,²⁰ or $\text{Ni}(\text{tfadt})_2^-$ complexes²¹ (Chart 1b) were able to engage in secondary coordination with $\text{M} \text{L}_n$ metal centers, forming extended chains through $-\text{CN} \cdots \text{M} \text{L}_n \cdots$ coordination (Chart 1c), as, for example, with $\text{Na}(18\text{-crown-6})^+$ cations,²¹ Mn^{III} metal ions of $\text{Mn}(\text{tetraphenylporphyrin})^+$,²² $\text{Cu}[\text{bis}(\text{ethylenediamine})]^{2+,23}$ or trimetallic $[\text{Cu}_2\text{Ln}]^{3+}$ tectons.²⁴ In all

cases however, *antiferromagnetic* interactions were systematically observed, either between overlapping $[\text{Ni}(\text{dithiolene})_2]^-$ anions²⁴ or between $[\text{Ni}(\text{dithiolene})_2]^-$ and the paramagnetic metal center.^{21,22} Other reported examples of dithiolene complexes with secondary coordination ability involve pyridine,²⁵ diazafluorene,²⁶ pyrazine,²⁷ or oxalate²⁸ moieties but exhibit, when possible, only antiferro- or ferrimagnetic²⁸ spin organizations.

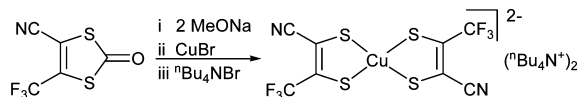
The Ni^{II} complex $[\text{Ni}(\text{cyclam})]^{2+}$ also offers two apical coordination sites for the formation of chains with bidentate ligands.²⁹ Its salts with paramagnetic anionic complexes such as $[\text{Cr}(\text{CN})_6]^{3-}$,³⁰ or $[\text{Fe}(\text{CN})_6]^{3-}$,³¹ exhibit a variety of one- or two-dimensional structures, characterized by a ferromagnetic coupling between the polycyanometallate and the $S = 1$ $[\text{Ni}(\text{cyclam})]^{2+}$ cation. It was therefore tempting to also evaluate the ability of radical molecules with coordinating nitrile substituents to similarly coordinate the $[\text{Ni}(\text{cyclam})]^{2+}$ with potentially intermolecular ferromagnetic interactions. This approach has been attempted by Ballester et al.³² with the organic radical anion TCNQ^- , but in $[\text{Ni}(\text{cyclam})][\text{TCNQ}]_2$, two TCNQ^- are needed to equilibrate the dicationic charge of $[\text{Ni}(\text{cyclam})]^{2+}$, affording $\cdots[\text{Ni}(\text{cyclam})]^{2+}[\text{TCNQ}]_2^{2-} \cdots$ chains with antiferromagnetically coupled diamagnetic $[\text{TCNQ}]_2^{2-}$ dimers linking the $[\text{Ni}(\text{cyclam})]^{2+}$ moieties. It was also reported with $[\text{Ni}(\text{mnt})_2]^{2-}$ in $[\text{Ni}(\text{cyclam})(\text{dmsO})_2][\text{Ni}(\text{mnt})_2]$, but as expressed by the salt formulation, the coordination sphere of the $[\text{Ni}(\text{cyclam})]^{2+}$ moiety was completed with two dmsO molecules rather than with the nitrile substituents of the dithiolene complex.³³

To avoid this recurrent antiferromagnetic coupling observed with $(\text{TCNQ})_2^{2-}$ dimers or with nickel $[\text{Ni}(\text{dithiolene})_2]$ complexes, we therefore envisioned the analogous copper(II) dithiolene complexes, $[\text{Cu}(\text{dithiolene})_2]^{2-}$. These copper complexes have not been investigated to such an extent as

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Scheme 1



the Ni/Pt/Pd triad complexes, but they exhibit two important characteristics: (i) a $S = 1/2$ spin state associated with a formal d^9 state for the copper and (ii) a dianionic character which is only stable with the most electron-withdrawing substituents on the two dithiolate ligands ($-\text{CN}$, $-\text{CF}_3$). The formal oxidation state of the copper ion in these dianionic copper complexes such as $[\text{Cu}(\text{mnt})_2]^{2-}$ has been already investigated from the determination of the S character from ^{33}S EPR superhyperfine data analysis³⁴ and confirmed recently by a combination of Cu L-edge and S K-edge X-ray absorption spectroscopies and DFT calculations, demonstrating a sizable contribution of the sulfur atoms to the singly occupied molecular orbital (SOMO).^{35,36} The analogy of the tfadt ligand used here with the mnt and tfd ones lets us infer a very similar behavior for $[\text{Cu}(\text{tfadt})_2]^{2-}$.

We decided to investigate the incorporation of dianionic $\text{Cu}(\text{dithiolate})_2^{2-}$ copper complexes in coordination chains with for example the dicationic $\text{Ni}(\text{cyclam})^{2+}$ complex to possibly afford neutral chains involving the $[\text{Cu}(\text{dithiolene})_2]^{2-}$ and $\text{Ni}(\text{cyclam})^{2+}$ species. Only one single example of a $[\text{Cu}(\text{mnt})_2]^{2-}$ species coordinated to a nickel macrocyclic dicationic species has been mentioned so far but without any magnetic interaction between the paramagnetic species in the discrete binuclear NiCu complex.³⁷ We describe here the original synthesis and X-ray crystal structure of the copper tfadt derivative, that is, $\text{Cu}(\text{tfadt})_2^{2-}$ as $n\text{-Bu}_4\text{N}^+$ salt and its metathesis with $[\text{Ni}(\text{cyclam})](\text{BPh}_4)_2$ to afford the neutral, crystalline salt $[\text{Ni}(\text{cyclam})][\text{Cu}(\text{tfadt})_2]$, with an analysis of its crystallographic and magnetic properties, characterized by an unprecedented ferromagnetic coupling between $S = 1/2$ and $S = 1$ species within heterobimetallic chains incorporating a formally d^9 copper dithiolene complex. This ferromagnetic coupling was further confirmed and explained thanks to theoretical calculations.

Results

Syntheses and Structural Properties. $[n\text{-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$ was prepared as described for the analogous nickel complex²¹ from the corresponding dithiocarbonate, 4-cyano-5-(trifluoromethyl)-1,3-dithiole-2-one, upon reaction with MeONa in MeOH, addition of CuBr followed by $n\text{-Bu}_4\text{NBr}$,

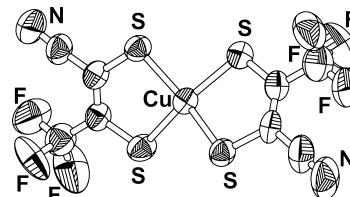


Figure 1. ORTEP view of the dianionic $[\text{Cu}(\text{tfadt})_2]^{2-}$ in its $n\text{-Bu}_4\text{N}^+$ salt, determined at room temperature. Thermal ellipsoids are drawn at the 50% probability level. Only one of the two disordered positions of the CF_3 groups has been shown for clarity.

and recrystallization from EtOH (Scheme 1). Cyclic voltammetry performed in 0.1 M CH_2Cl_2 with $n\text{-Bu}_4\text{NPF}_6$ as electrolyte shows that $[n\text{-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$ exhibits a reversible oxidation wave at -0.42 V vs Fc^+/Fc to the monoanionic, d^8 species. Note that, for the analogous $[\text{Cu}(\text{mnt})_2]^{2-}$ system, the reversible $-2/-1$ wave was observed at 0.01 V vs Fc^+/Fc (0.41 V vs SCE),^{38,39} illustrating the weaker electron withdrawing effect of the CF_3 moiety, when compared to that of the nitrile one. This reversible redox process is followed by an irreversible process with $E_{\text{ox}} = 0.797$ and $E_{\text{red}} = 0.031$ V vs Fc^+/Fc .

$[n\text{-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$ crystallizes in the monoclinic system, space group $P2_1/n$, with both ions in a general position in the unit cell (Figure 1). Of particular note is the dihedral angle between the two metallacycles, which amounts here to $30.396(12)^\circ$, characteristic of the d^9 state. Indeed, this value is intermediate between those found in the d^{10} tetrahedral dithiolene complexes with Zn^{2+} or Hg_2^{2+} ($\theta \approx 90^\circ$) and in the d^8 square planar complexes ($\theta \approx 0^\circ$). Other geometrical characteristics are collected in Table 1.

In the solid state, the radical $[\text{Cu}(\text{tfadt})_2]^{2-}$ complexes are fully isolated from each other by the alkyl chains of the $n\text{-Bu}_4\text{N}^+$ cations. This is confirmed by the temperature dependence of the magnetic susceptibility, which follows a Curie law in the whole temperature range studied (1.8 – 300 K). It is worth noting also the trans configuration of the distorted square planar complex, a recurrent feature of these dithiolene complexes with such unsymmetrically substituted dithiolate ligands,^{20,21} and a stringent requirement for the formation of extended chains through CN coordination (Chart 1c).

Mixing $[n\text{-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$ with $[\text{Ni}(\text{cyclam})][\text{BPh}_4]_2$ in CH_3CN afforded after standing for a few days red crystals of the mixed salt formulated as $[\text{Ni}(\text{cyclam})][\text{Cu}(\text{tfadt})_2]$. It crystallizes in the monoclinic system, space group $P2_1/n$, with both dication and dianion located on inversion centers (Figure 2). As a consequence of these crystallographic characteristics, the dithiolene complex adopts now: (i) a trans conformation and (ii) a perfect square-planar geometry with $\theta = 0^\circ$ despite its d^9 state, illustrating the flexibility of those complexes, also observed in other $[\text{M}(\text{tfadt})_2]^{2-}$ complexes.^{21,41} On the other hand, the CuS_2C_2 metallacycle is not planar but slightly folded along the S–S hinge by $8.49(9)^\circ$. Other geometrical characteristics are collected in Table 1. The

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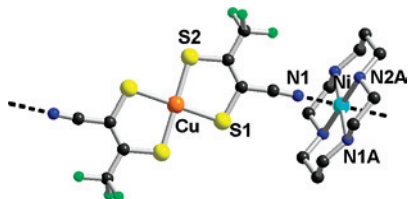
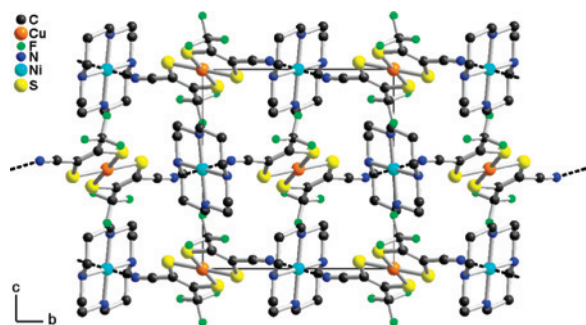
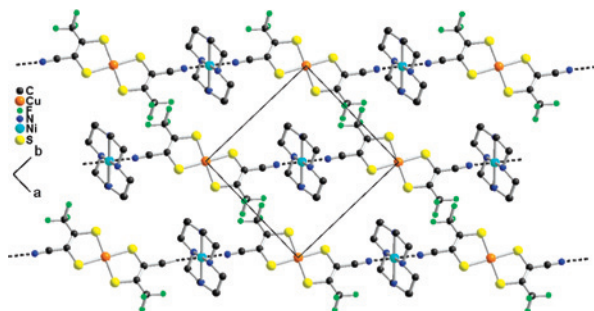
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Table 1. Geometrical Characteristics of Copper Dithiolene Complexes (in Å unless otherwise stated)

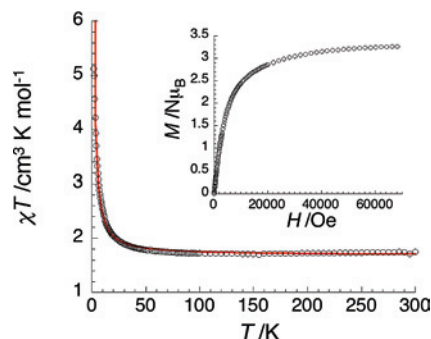
compound	Cu–S(CN)	Cu–S(CF ₃)	S–C(CN)	S–C(CF ₃)	C=C	θ (deg)	ref
[Cu(tfadt) ₂] ^{2–a}	2.2529(15)	2.2503(15)	1.737(5)	1.716(5)	1.354(7)	30.38(6)	<i>d</i>
	2.2490(15)	2.2547(16)	1.739(6)	1.711(6)	1.349(7)		
[Cu(tfadt) ₂] ^{–b}	2.2657(11)	2.2539(11)	1.734(4)	1.721(4)	1.369(6)	0.0	<i>d</i>
[Cu(mnt) ₂] ^{–c}	2.269(1)		1.724(4)		1.357(4)	0.0	40
	2.286(1)		1.726(3)				

^a As *n*-Bu₄N⁺ salt. ^b As [Ni(cyclam)]²⁺ salt. ^c As Ph₄P⁺ salt. ^d This work.


Figure 2. View of the chains in [Ni(cyclam)][Cu(tfadt)₂]. Hydrogen atoms on the cyclam ring have been omitted for clarity.

Figure 3. Projection view along *a* of the unit cell of [Ni(cyclam)][Cu(tfadt)₂], showing the absence of any direct intermolecular dithiolene/dithiolene interactions in the *b,c* plane.

Figure 4. Projection view along *c* of the *a,b* layer with heterobimetallic chains running along *a+b* showing the absence of any direct intermolecular dithiolene/dithiolene interactions in the *a,b* plane.

[Ni(cyclam)]²⁺ moiety adopts the usual conformation with Ni···N distances of 2.075(4) and 2.077(3) Å for Ni···N1A and Ni···N2A, respectively. The coordination around the nickel atom is completed by two nitrile groups of the [Cu(tfadt)₂]^{2–} moieties with a Ni···N1 distance of 2.133(3) Å, giving rise to an elongated octahedral environment for the Ni^{II} metal ions.

As shown in Figures 3 and 4, this coordination of the [Ni(cyclam)]²⁺ moieties through the nitrile substituents of the dithiolene complexes gives rise to the formation of heterobimetallic chains of alternating [Ni(cyclam)]²⁺ and [Cu(tfadt)₂]^{2–} running along the *a+b* and *a–b* directions. A projection view of the unit cell along *a* (Figure 3) and a view of one *a,b* layer along *c* (Figure 4) show how the copper dithiolene complexes are pushed apart from each other, hindering any possibility for direct overlap between the


Figure 5. Temperature dependence of the χT product at 1000 Oe for 2 (with $\chi = M/H$ normalized per mol). The red solid line shows the best fit obtained with the chain model described in the text. Inset: M vs H plot at 1.8 K. See also Figure S1 for detail on the low-temperature region.

dianionic complexes, thus leaving the chains well isolated from each other.

Magnetic Properties. Temperature dependence of the magnetic susceptibility has been determined down to 1.8 K, and the χT vs T plot at 1000 Oe is reported in Figure 5. The steady increase of the χT product upon lowering the temperature indicates the presence of dominant ferromagnetic interactions. On the basis of the structure of this compound, the magnetic susceptibility has been fitted down to 1.8 K to an isotropic alternating chain model of ferromagnetically coupled quantum $S = 1/2$ and classical $S = 1$ spins.^{42,43} The best set of parameters obtained is $J/k_B = +5.0(2)$ K and $g = 2.22(5)$. As expected for Ni(II) centers in a distorted octahedral coordination sphere, the g value is significantly higher than 2.0. The magnetization at 1.83 K (Figure 5) is saturated around 3.3 μ_B , confirming the ferromagnetic interaction between Ni(II) and [Cu(tfadt)₂] spin carriers. It is worth noting that attempts to detect slow relaxation of the magnetization, that is, single-chain magnet behavior,^{18,19} have been unsuccessful above 1.8 K most likely due to the lack of a significant magnetic anisotropy in this system.

Discussion

To compare with the experimental result deduced from the susceptibility measurements, we also used a computational approach to evaluate the coupling constant between the two paramagnetic centers in the chain. A method based on the density functional theory,⁴⁴ with the B3LYP hybrid functional,⁴⁵ as implemented in the Gaussian03 code,⁴⁶ and a triple- ζ quality basis set proposed by Ahlrichs et al. has

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(43) The corresponding Hamiltonian writes as $H = -2J\sum_i((S_i + S_{i+1}) \times s_i)$ where S_i is the classical spin ($S = 1$) and s_i is the quantum spin ($S = 1/2$).

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been employed.⁴⁷ Among the existing theoretical approaches,^{48,49} the exchange coupling constant was obtained as the direct energy difference between the high spin state and a broken-symmetry wave function for the low spin state, as proposed by Noodleman et al.⁴⁹ and further described by Ruiz et al.,⁵⁰ giving excellent results with the B3LYP method for the reckoning of the coupling constants.⁵¹ The relationship used to obtain the coupling constant from the energy of the broken-symmetry state (E_{BS}) and from the high spin state (E_{HS}), where S_{Cu} and S_{Ni} represent the local spin on the metal centers, is

$$J = \frac{E_{BS} - E_{HS}}{2S_{Cu}S_{Ni} + S_{Cu}} = \frac{2}{3}(E_{BS} - E_{HS})$$

We considered here a trimer unit of $\{[Cu(tfadt)][Ni(cyclam)]-[Cu(tfadt)]\}^{2-}$ as a model for the chain. With the trivial high spin state where all local spins have the same orientation, two different low spin configurations were evaluated. They were constructed by the inversion of only one local spin, of either Cu^{II} or Ni^{II} . Only one broken-symmetry distribution is needed, but the extra broken-symmetry configuration serves as verification. The calculated exchange interaction is effectively found to be ferromagnetic with a value of $J/k_B = +7.3$ K, in extremely good agreement with the value deduced from the experimental data by the Seiden model (+5.0 K). To rationalize the origin of the ferromagnetic interaction, we can use the Kahn-Briat model⁵² which relates the antiferromagnetic contribution of the exchange coupling constant with the overlap between the orbitals bearing the unpaired electrons. For a square planar Cu^{II} cation ($S = 1/2$) and an octahedral Ni^{II} cation ($S = 1$), the unpaired electrons of both dication and dianion are expected to be in e_g symmetry orbitals; hence, one would expect an antiferro-

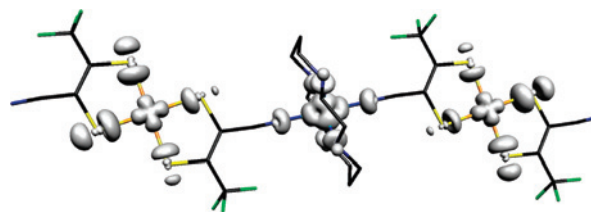


Figure 6. Spin density distribution for $\{[Cu(tfadt)][Ni(cyclam)]-[Cu(tfadt)]\}^{2-}$ corresponding to the high spin ground state. The isodensity surface represented corresponds to a value of $0.005 e^-/\text{bohr}^3$.

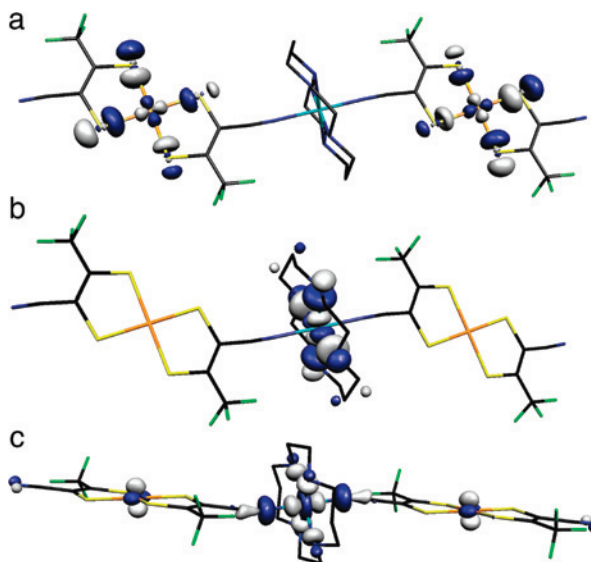


Figure 7. Representation of three singly occupied magnetic orbitals for $\{[Cu(tfadt)][Ni(cyclam)]-[Cu(tfadt)]\}^{2-}$ corresponding to the high spin ground state.

magnetic interaction. The spin density distribution obtained from the computational approach (Figure 6) indicates indeed that the unpaired electron centered on the Cu^{II} cation is in a $d_{x^2-y^2}$ orbital mainly delocalized over the copper and the four sulfur atoms (see Figure 7a), in accordance with earlier experimental and theoretical results³⁵ reported on $[Cu(mnt)_2]^{2-}$. On the other hand, the two unpaired electrons of the $Ni(cyclam)$ moiety correspond to the $d_{x^2-y^2}$ and d_{z^2} orbitals (see Figure 7b,c). Because of the axial coordination, the two “singly occupied magnetic orbitals” (SOMO) of $d_{x^2-y^2}$ symmetry are orthogonal, and the only possible antiferromagnetic contribution then corresponds to the overlap of the SOMO centered on the Cu^{II} and the d_{z^2} like SOMO centered on the Ni^{II} . However, no spin density is observed on the three carbon atoms of the dithiolate ligand (Figure 6), because both the $d_{x^2-y^2}$ symmetry of the copper dithiolene and the d_{z^2} of the nickel frontier orbitals are associated with a sigma overlap that vanishes rapidly with the distance.

Therefore, the overlaps between the SOMOs of the $Cu(tfadt)$ and $Ni(cyclam)$ moieties are either null or really small, affording in the end the ferromagnetic interaction experimentally observed, despite the fact that the SOMOs of the two moieties have the same e_g configuration. This behavior contrasts strongly with the salts of $[Ni(cyclam)]^{2+}$ with $[Cr(CN)_6]^{3-}$ or $[Fe(CN)_6]^{3-}$ mentioned in the Introduction.^{30,31} Indeed, the ferromagnetic interaction observed in

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these salts derives, as expected,^{53,54} from the symmetry orthogonality of the t_{2g}^3 (Cr^{III}) or t_{2g}^5 (Fe^{III}) orbitals with the e_g^2 orbitals of the $[\text{Ni}(\text{cyclam})]^{2+}$ fragment. In the present case, the nontrivial ferromagnetic interaction between e_g^2 $[\text{Ni}(\text{cyclam})]^{2+}$ and e_g^1 $[\text{Cu}(\text{tfadt})_2]^{2-}$ arises from the axial coordination in one hand and from the peculiar character of the copper dithiolene complex on the other hand. Indeed, in the formally d^7 Ni complexes, the SOMO has a π character and delocalizes extensively through the π system to the nitrile substituents, allowing for an antiferromagnetic interaction, as observed, for example, in the chains $[\text{Mn}(\text{tpp})][\text{Ni}(\text{mnt})_2]$ or $[\text{Mn}(\text{tpp})][\text{Ni}(\text{adt})_2]$.²² In the d^9 copper complexes, the SOMO of $d_{x^2-y^2}$ symmetry is orthogonal to the π system and limited to the CuS_4 core of the complex.

Conclusions

We have described here a novel paramagnetic ($S = 1/2$) copper dithiolene complex based on the tfadt ligand and demonstrated its ability to connect $[\text{Ni}(\text{cyclam})]^{2+}$ moieties into infinite, one-dimensional heterobimetallic chains through $\text{CN}\cdots\text{Ni}$ interactions. Two chain orientations are found, without any short intermolecular distances between the dithiolene complexes. This leaves the chains independent from each other and hinders any direct antiferromagnetic overlap between the dithiolene complexes, a recurrent feature in most salts of dithiolene complexes examined so far. The axial coordination, combined with the $d_{x^2-y^2}$ symmetry of the $[\text{Cu}(\text{tfadt})_2]^{2-}$ frontier orbital, allows for an unprecedented ferromagnetic interaction despite the common e_g symmetry of interacting orbitals. A very good agreement was found between the experimental exchange interaction deduced from the fit of the magnetic susceptibility ($J_{\text{exp}}/k_B = +5.0$ K) and that calculated on a model trimeric motif ($J_{\text{calc}}/k_B = +7.3$ K). This attractive symmetry property of the d^9 copper dithiolene complexes is not restricted to the tfadt ligand, and analogous copper complexes with other dithiolene ligands blessed with secondary coordination ability are being investigated now to take advantage of this ferromagnetic interaction, in particular in the design of new single-chain magnet systems.

Experimental Section

Synthesis. $[\text{n-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$. 4-Cyano-5-trifluoromethyl-1,3-dithiole-2-one²¹ (0.25 g, 1.18 mmol) was added to a freshly prepared solution of sodium (0.065 g, 2.8 mmol) in MeOH (5 mL). The resulting green solution was stirred under N_2 for 45 min, and CuCl (0.058 g, 0.59 mmol) was added to give a red solution into which $[\text{n-Bu}_4\text{N}]\text{Br}$ (0.57 g, 1.76 mmol) was added. After stirring for 1.5 h, water (80 mL) was added and the red-brown precipitate filtered, washed with water, and dried by suction. Recrystallization in EtOH yielded $[\text{n-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$ as red brown needles (0.25 g, 0.27 mmol, 47%). Anal. Calcd for $\text{C}_{40}\text{H}_{72}\text{F}_6\text{N}_4\text{CuS}_4$: C, 52.51; H, 7.93; N, 6.12. Found: C, 52.27; H, 7.87; N, 6.06.

$[\text{Ni}(\text{cyclam})][\text{Cu}(\text{tfadt})_2]$. $\text{Ni}(\text{cyclam})(\text{BPh}_4)_2$ (20 mg, 0.024 mmol) was dissolved in distilled CH_3CN (3 mL), and solid

Table 2. Crystallographic Data

compound	$[\text{n-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$	$[\text{Ni}(\text{cyclam})][\text{Cu}(\text{tfadt})_2]$
formula	$\text{C}_{40}\text{H}_{72}\text{CuF}_6\text{N}_4\text{S}_4$	$\text{C}_{18}\text{H}_{24}\text{CuF}_6\text{N}_6\text{Ni S}_4$
FW ($\text{g}\cdot\text{mol}^{-1}$)	914.8	688.92
crystal color	red-brown	red
crystal shape	needle	needle
crystal size (mm)	$0.58 \times 0.14 \times 0.04$	$0.43 \times 0.059 \times 0.056$
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
T (K)	293(2)	293(2)
a (Å)	15.2546(15)	10.5773(12)
b (Å)	22.2558(16)	10.8899(11)
c (Å)	15.7617(12)	11.4306(9)
β (deg)	112.426(10)	97.292(8)
V (Å ³)	4946.5(7)	1306.0(2)
Z	4	2
D_{calc} ($\text{g}\cdot\text{cm}^{-3}$)	1.228	1.742
ν (mm^{-1})	0.663	1.918
total reflns	38818	8854
unique reflns (R_{int})	9406	2975
unique reflns ($I > \sigma(I)$)	2789	1908
R_1, wR_2 ($I > 2\sigma(I)$)	0.0437, 0.0658	0.0416, 0.1088
R_1, wR_2 (all data)	0.1852, 0.0959	0.0823, 0.1288
goodness-of-fit	0.708	1.090

$[\text{n-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$ (20.5 mg, 0.024 mmol) was added. The red solution was allowed to stand two days during which red needles appeared. They were filtered and suspended overnight in CH_2Cl_2 to remove a white impurity. Filtration afforded the title compound (10 mg, 0.0145 mmol, 66.6%) as red needles. Calcd for $\text{C}_{18}\text{CuH}_{24}\text{F}_6\text{N}_6\text{NiS}_4$: C, 31.38; H, 3.51; N, 12.20. Found: C, 31.45; H, 3.21; N, 12.24.

Crystallography. Crystals were mounted on top of a thin glass fiber. Data for $[\text{n-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$ were collected on a Stoe Imaging Plate Diffraction System (IPDS) and on an Enraf-Nonius Kappa-CCD diffractometer for $[\text{Ni}(\text{cyclam})][\text{Cu}(\text{tfadt})_2]$, both with graphite-monochromatized $\text{Mo K}\alpha$ radiation, $\lambda = 0.71073$ Å. The crystal data are summarized in Table 2. Structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods (SHELXL-97). Absorption corrections were applied for both structures. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined. The structure of $[\text{n-Bu}_4\text{N}]_2[\text{Cu}(\text{tfadt})_2]$ was affected by disorder, on two butyl chains as well as on the CF_3 groups.

Magnetic Measurements. The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. M vs H measurements have been performed at 100 K to check for the presence of ferromagnetic impurities that has been found absent. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

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Supporting Information Available: Crystal data as CIF files and Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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