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Dithiolene complexes as metalloligands: $[\text{Cu}(\text{en})_2][\text{Cu}(\text{mnt})_2]$, an $S = \frac{1}{2}$ spin chain

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ARTICLE INFO

Article history:

Received 11 January 2012

Accepted 6 April 2012

Available online 4 June 2012

Keywords:

S ligands

Magnetic properties

Copper

Structure elucidation

Through-space interactions

Mots clés :

S-ligands

Propriétés magnétiques

Cuivre

Résolution structurale

Interactions à travers l'espace

ABSTRACT

The paramagnetic dithiolene complex $[\text{Cu}(\text{mnt})_2]^{2-}$ (mnt: 1,2-dicyanoethylene-1,2-dithiolate) is used as metalloligand for coordination of dicationic $[\text{Cu}(\text{en})_2]^{2+}$ (en: ethylenediamine) complex, leading to the formation of chains of alternating $[\text{Cu}(\text{mnt})_2]^{2-}$ and $[\text{Cu}(\text{en})_2]^{2+}$ moieties through $\text{C}\equiv\text{N}\bullet\bullet\bullet\text{Cu}\bullet\bullet\bullet\text{N}\equiv\text{C}$ *trans* coordination with $\text{N}\bullet\bullet\bullet\text{Cu}$ distance of 2.664(4) Å and a noticeable deviation from linearity as the $\text{C}\equiv\text{N}\bullet\bullet\bullet\text{Cu}$ angle amounts to 146.3(3)°. The $[\text{Cu}(\text{en})_2][\text{Cu}(\text{mnt})_2]$ salt exhibits weak antiferromagnetic interactions between spin carriers along the chains and slightly stronger inter-chain $[\text{Cu}(\text{mnt})_2]\bullet\bullet\bullet[\text{Cu}(\text{mnt})_2]$ antiferromagnetic interactions through intermolecular $\text{S}\bullet\bullet\bullet\text{S}$ contacts.

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R É S U M É

Le complexe dithiolène paramagnétique $[\text{Cu}(\text{mnt})_2]^{2-}$ (mnt: 1,2-dicyanoéthylène-1,2-dithiolate) est utilisé comme métalloligand pour la coordination du complexe dicationique $[\text{Cu}(\text{en})_2]^{2+}$ (en: éthylènediamine), conduisant ainsi à la formation de chaînes alternant les complexes $[\text{Cu}(\text{mnt})_2]^{2-}$ et $[\text{Cu}(\text{en})_2]^{2+}$ grâce à une coordination axiale $\text{C}\equiv\text{N}\bullet\bullet\bullet\text{Cu}\bullet\bullet\bullet\text{N}\equiv\text{C}$, caractérisée par une distance $\text{N}\bullet\bullet\bullet\text{Cu}$ de 2.664(4) Å et une déviation importante à la linéarité, comme le montre l'angle $\text{C}\equiv\text{N}\bullet\bullet\bullet\text{Cu}$ à 146.3(3)°. Le sel $[\text{Cu}(\text{en})_2][\text{Cu}(\text{mnt})_2]$ présente (i) des interactions antiferromagnétiques faibles entre porteurs de spin le long de la chaîne et (ii) des interactions antiferromagnétiques $[\text{Cu}(\text{mnt})_2]\bullet\bullet\bullet[\text{Cu}(\text{mnt})_2]$ plus fortes entre chaînes via des contacts $\text{S}\bullet\bullet\bullet\text{S}$.

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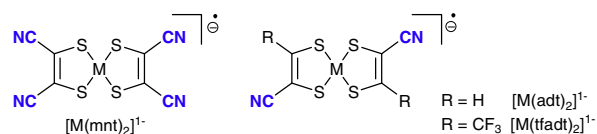
1. Introduction

In the field of molecule-based magnetism, one-dimensional magnetic systems have attracted attention for many years [1]. The discoveries of bimetallic chain compounds [2] and polymeric transition metal complexes with bridging nitronylnitroxide radical ligands [3] exemplify

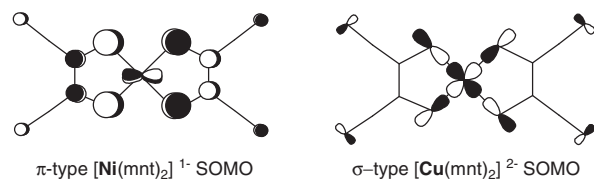
how modern coordination chemists are able to design matter at the molecular level to synthesize magnetic one-dimensional compounds to model and experimentally illustrate basic physic problems such as coupling mechanisms between different spin carriers or the effect of low-dimensionality on the magnetic properties. More recently, Single-Chain Magnets (SCM) [4,5] in which ferro-, ferrimagnetic or uncompensated canted spin configurations along the chains are associated with a large magnetic anisotropy, also raised a strong interest and an active research topic. In this context, paramagnetic dithiolene

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Scheme 1.

Scheme 2. The contrasted characteristics of the SOMO of the π -type $[\text{Ni}(\text{mnt})_2]^{-1}$ and σ -type $[\text{Cu}(\text{mnt})_2]^{2-}$ radical species. Adapted from ref. [14c].

complexes were rarely investigated as *paramagnetic bridging coordinating* centers between transition metal complexes in the same way nitronylnitroxides do through $\text{N}-\text{O}\cdots\text{ML}_n\cdots$ interactions. For example, the nitrile moieties of paramagnetic complexes such as $[\text{Ni}(\text{mnt})_2]^{-1}$, $[\text{Ni}(\text{adt})_2]^{-1}$ [6], or $[\text{Ni}(\text{tfadt})_2]^{-1}$ complexes [7] (Scheme 1) are able to engage in secondary coordination with ML_n metal centers, forming extended chains through $-\text{CN}\cdots\text{ML}_n\cdots$ coordination, as for example with $\text{Na}(18\text{-crown-6})^+$ cations [7], Mn^{III} metal ions of $\text{Mn}(\text{tetraphenylporphyrin})^+$ [8], $[\text{Cu}(\text{bis}(\text{ethylenediamine}))_2]^{2+}$ [9] or trimetallic $[\text{Cu}_2\text{Ln}]^{3+}$ tectons [10].

In all cases, *antiferromagnetic* interactions were systematically observed, either between overlapping $[\text{Ni}(\text{dithiolene})_2]^{-1}$ radical anions [10], or between $[\text{Ni}(\text{dithiolene})_2]^{-1}$ and the paramagnetic metal center [7,8]. In these salts, the SOMO of the paramagnetic dithiolene complex, $[\text{Ni}(\text{dithiolene})_2]^{-1}$, is the out-of-phase combination of the two dithiolate ligand orbitals with a Nickel d orbital, giving this SOMO a π -type character, with strong delocalization on the ligands (Scheme 2) [11,12]. Recent calculations give a 40% residual spin density on the nickel atom. If one moves from the group 10 nickel complexes to the group 11 copper complexes, the SOMO of the dianionic copper complexes, formulated as $[\text{Cu}(\text{dithiolene})_2]^{2-}$, is now built out of the $d_{x^2-y^2}$ copper orbital interacting with thiolate moieties, giving this frontier orbital a σ -type character [13,14]. It is therefore anticipated that interactions of either the formally d^7 nickel anionic complexes or the d^9 copper dianionic complexes, with other metallic centers through secondary coordination, should lead to totally different magnetic interactions despite similar coordination patterns. Note that in both cases, the nitrogen lone pair of the nitrile is not engaged in the SOMO, implying that magnetic interactions through coordination will be always weak.

We have recently disclosed that the nitrile-containing paramagnetic copper complex⁶ $[\text{Cu}(\text{tfadt})_2]^{2-}$ was able to coordinate $[\text{Ni}(\text{cyclam})]^{2+}$ species through two *trans* $\text{CN}\cdots\text{Ni}$ interactions leading to the formation of alternated $S = 1/S = 1/2$ spin chains with *ferromagnetic* interactions. In our following attempts to prepare other such systems, we have successfully isolated and characterized an

Table 1
Selected bond distances and angles in $[\text{Cu}(\text{en})_2][\text{Cu}(\text{mnt})_2]$.

$[\text{Cu}(\text{mnt})_2]^{2-}$		$[\text{Cu}(\text{en})_2]^{2+}$	
Bond distances (Å)			
Cu1–S1	2.2616(10)	Cu2–N1A	1.998(3)
Cu1–S2	2.2739(10)	Cu2–N2A	2.015(3)
S1–C1	1.727(4)	N1A–C2A	1.477(5)
S2–C3	1.733(3)	N2A–C1A	1.475(5)
C1–C3	1.360(5)	C1A–C2A	1.495(5)
Bond angles (°)			
S1–Cu1–S2	90.76(4)	N1A–Cu2–N2A	84.22(12)
Cu1–S1–C1	101.55(12)	Cu2–N1A–C2A	110.3(2)
Cu1–S2–C3	101.59(13)	Cu2–N2A–C1A	108.8(2)
S1–C1–C3	122.5(3)	N1A–C2A–C1A	108.5(3)
S2–C3–C1	122.8(3)	N2A–C1A–C2A	108.4(3)

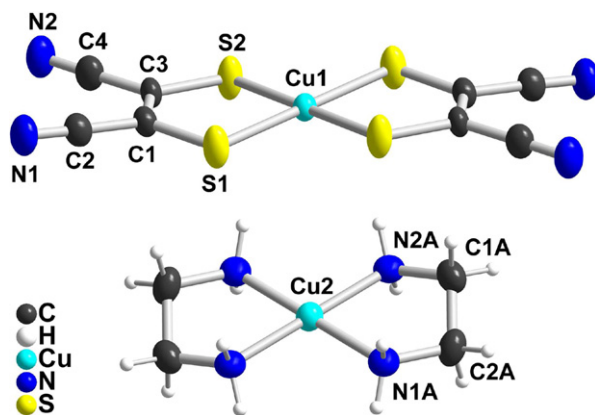
analogous salt involving $[\text{Cu}(\text{en})_2]^{2+}$ as dication and $[\text{Cu}(\text{mnt})_2]^{2-}$ as dianion which organizes into chains through two *trans* $\text{CN}\cdots\text{Cu}$ interactions, as detailed below.

2. Results and discussion

2.1. Syntheses and structure

The preparation of the title compound is based on the metathesis reaction between $[\text{nBu}_4\text{N}]_2[\text{Cu}(\text{mnt})_2]$ with $[\text{Cu}(\text{en})_2](\text{BF}_4)_2$ in CH_3CN . Crystals were obtained after partial evaporation of the mixed solutions. The salt crystallizes in the monoclinic system, space group $P2_1/c$, with both dicationic and dianionic complexes located on inversion centers (Fig. 1). Intramolecular bond distances and angles are collected in Table 1.

In the solid state, the dicationic and dianionic moieties are organized into layers, perpendicular to the c axis (Fig. 2). Within a layer, we observe the formation of chains through the coordination of the $\text{Cu}(\text{II})$ center in $[\text{Cu}(\text{en})_2]^{2+}$ by the nitrile substituent of the *mnt* ligand of the $[\text{Cu}(\text{mnt})_2]^{2-}$ unit with a $\text{N}(1)\cdots\text{Cu}(2)$ distance of 2.664(4) Å (Fig. 3). The coordination deviates from linearity as the $\text{C}\equiv\text{N}\cdots\text{Cu}$ angle amounts to 146.3(3)°. As a consequence, the magnetic interaction between the two

Fig. 1. ORTEP drawing of (a) $[\text{Cu}(\text{mnt})_2]^{2-}$ and (b) $[\text{Cu}(\text{en})_2]^{2+}$ moieties with the selected atom-labeling schemes and thermal ellipsoids at 50% probability.

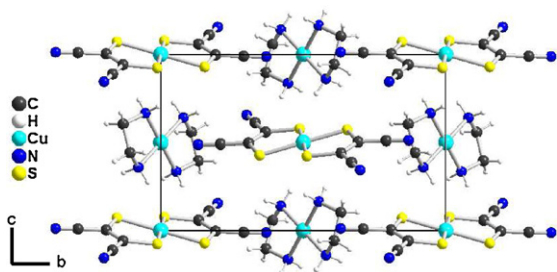


Fig. 2. View of the unit cell of $[\text{Cu}(\text{en})_2][\text{Cu}(\text{mnt})_2]$ projected in the bc plane.

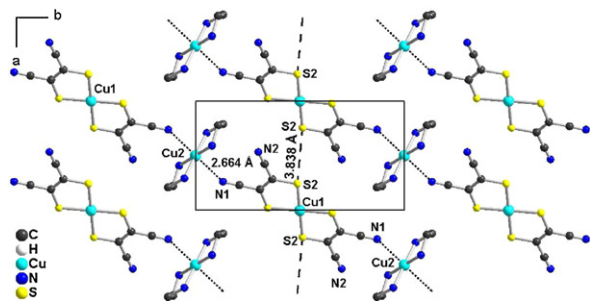


Fig. 3. View of the coordination chains running along $(a+b)$ in $[\text{Cu}(\text{en})_2][\text{Cu}(\text{mnt})_2]$ projected in the ab plane. Hydrogen atoms were omitted for clarity.

spin carriers through this $\text{C}\equiv\text{N}\cdots\text{Cu}$ coordination is expected to be very weak. Furthermore, as a sizeable part of the spin density is delocalized on the sulfur atoms in $[\text{Cu}(\text{mnt})_2]^{2-}$, intermolecular $\text{S}\cdots\text{S}$ contacts might also provide paths for direct exchange interactions. The shortest $\text{S}\cdots\text{S}$ contact, $\text{S}(2)\cdots\text{S}(2) = 3.84(2)$ Å, is close to van der Waals contact distance and would lead to the formation of uniform spin chain running along a (Fig. 3).

2.2. Magnetic properties

The temperature dependence of the magnetic susceptibility is given on Fig. 4 as χT product vs. T plot. As a first approach and based on the structure of this compound, the magnetic susceptibility has been modeled taking into account only the coordination chain formed by alternating $[\text{Cu}(\text{mnt})_2]^{2-}$ and $[\text{Cu}(\text{en})_2]^{2+}$ units. Therefore an isotropic regular chain model of $S = \frac{1}{2}$ quantum spins has been used to fit the experimental data with the following spin Hamiltonian: $H = -2J\sum S_i S_{i+1}$ with J being the intra-chain magnetic interaction between $[\text{Cu}(\text{mnt})_2]^{2-}$ and $[\text{Cu}(\text{en})_2]^{2+}$ spin carriers [2]. The best set of parameters obtained considering the experimental data down to 10 K is $J/k_B = -3.8(5)$ K and $g = 2.02(5)$ (note that this last value is significantly higher than 2 as expected for Cu(II) centers). As shown on Fig. 4 (red line), this model is not able to reproduce the data below 10 K, leading to a theoretical χT product much lower than experimentally observed. Furthermore, the introduction of antiferromagnetic inter-chain interaction (through intermolecular $\text{S}\cdots\text{S}$ contacts between $[\text{Cu}(\text{mnt})_2]$ anions) cannot improve the quality of

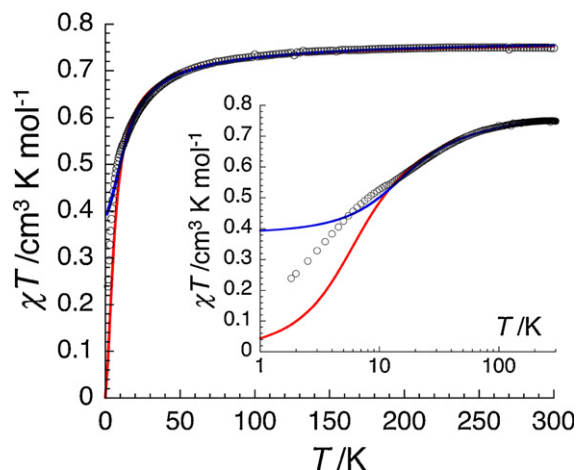


Fig. 4. Temperature dependence of the χT product at 1000 Oe for $[\text{Cu}(\text{en})_2][\text{Cu}(\text{mnt})_2]$ (with χ defined as the molar magnetic susceptibility equal to M/H per $[\text{Cu}(\text{en})_2][\text{Cu}(\text{mnt})_2]$ unit) in linear (main) and semi-logarithm (inset) plots. Solid red and blue lines indicate the best fits obtained with the models described in the text.

the obtained model as it will only further lower the theoretical χT product.

This result demonstrates that the dominant antiferromagnetic interactions in this system are likely mediated by the $\text{S}\cdots\text{S}$ contacts between $[\text{Cu}(\text{mnt})_2]$ units and not between $[\text{Cu}(\text{mnt})_2]^{2-}$ and $[\text{Cu}(\text{en})_2]^{2+}$ units along the coordination chain. Hence, an alternative model has been used considering only the $[\text{Cu}(\text{mnt})_2]\cdots[\text{Cu}(\text{mnt})_2]$ antiferromagnetic interactions in the frame of an isotropic regular chain model of $S = \frac{1}{2}$ quantum spins (see the Hamiltonian above) and treating the $[\text{Cu}(\text{en})_2]^{2+}$ cations as a Curie contribution. Using this approach, the theoretical curve (Fig. 4, blue line) is able to reproduce the measured susceptibility down to 10 K with $J/k_B = -9.6(5)$ K and $g = 2.03(5)$. This time, the calculated χT product is closer and slightly higher than the experimental data below 10 K. This makes this approach more realistic considering that the presence of antiferromagnetic $[\text{Cu}(\text{en})_2]\cdots[\text{Cu}(\text{mnt})_2]$ interactions should further lower and adjust the estimated χT product. Unfortunately, an analytical 2D network model of $S = \frac{1}{2}$ quantum spins with two different J parameters is not available to further analyze these magnetic data. Nevertheless on the basis of the previous analyses, it can be speculated that the $[\text{Cu}(\text{mnt})_2]\cdots[\text{Cu}(\text{mnt})_2]$ antiferromagnetic interaction is likely falling in the -5 and -9 K range while the $[\text{Cu}(\text{en})_2]\cdots[\text{Cu}(\text{mnt})_2]$ coupling should not exceed -1 K.

In conclusion, the paramagnetic dithiolene complex $[\text{Cu}(\text{mnt})_2]^{2-}$ (mnt: 1,2-dicyanoethylene-1,2-dithiolate) has been coordinated to the dicationic $[\text{Cu}(\text{en})_2]^{2+}$ (en: ethylenediamine) complex to form chains of alternating $[\text{Cu}(\text{mnt})_2]^{2-}$ and $[\text{Cu}(\text{en})_2]^{2+}$ moieties through $\text{C}\equiv\text{N}\cdots\text{Cu}\cdots\text{N}\equiv\text{C}$ *trans* coordination. As shown by the magnetic susceptibility measurements and their analysis, the $[\text{Cu}(\text{en})_2][\text{Cu}(\text{mnt})_2]$ salt is better described as a two-dimensional magnetic network with dominating $[\text{Cu}(\text{mnt})_2]\cdots[\text{Cu}(\text{mnt})_2]$ antiferromagnetic interactions

through intermolecular S...S contacts and much weaker [Cu(en)₂] $\bullet\bullet\bullet$ [Cu(mnt)₂] antiferromagnetic interactions mediated by direct coordination.

3. Experimental

3.1. Synthesis

[Cu(en)₂Cu(mnt)₂]. A solution of [Cu(en)₂(BF₄)₂] [15] (10 mg, 0.028 mmol) in CH₃CN is mixed with a solution of (TBA)₂[Cu(mnt)₂] [16] (23 mg, 0.028 mmol) in CH₃CN (1 mL). Slow evaporation of half of the solvent yielded [Cu(en)₂Cu(mnt)₂] (10 mg, 0.019 mmol, 68%) as red brown platelets. Mp > 300 °C. Elem. Anal. Calcd. for C₁₂H₁₆Cu₂N₈S₄ (Found): C, 27.31 (27.57); H, 3.06 (3.03); N, 21.24 (21.38). IR (ATR): $\bar{\nu}_{\text{CN}} = 2198 \text{ cm}^{-1}$.

3.2. Crystallography

Single crystals were mounted on the top of a thin glass fiber. Data were collected on a Stoe IPDS-I diffractometer at room temperature with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Structures were solved by direct methods (SHELXS-97) and refined (SHELXL-97) by full-matrix least-squares methods, [17] as implemented in the WinGX software package [18]. Absorption corrections were applied. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined. Crystallographic data: C₁₂H₁₆Cu₂N₈S₄, $M = 527.65$, monoclinic, P2₁/c, $a = 7.8817(11)$, $b = 14.220(3)$, $c = 9.2313(13) \text{ \AA}$, $\beta = 108.464(16)^\circ$, $V = 981.4(3) \text{ \AA}^3$, $Z = 2$, $D_c = 1.786 \text{ g cm}^{-3}$, $T = 293(2) \text{ K}$, 9357 reflections collected, 1839 unique ($R_{\text{int}} = 0.0916$), $R_1 [I > 2\sigma(I)] = 0.0304$, $wR_2 (F, \text{all data}) = 0.0611$, $\text{GoF} = 0.803$. CCDC-862006 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

3.3. Magnetic characterizations

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. Measurements were performed on a polycrystalline sample of 28.06 mg introduced in a polyethylene bag ($3 \times 0.5 \times 0.02 \text{ cm}$). M vs H measurements has 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 calculated from the Pascal's constants [19].

Acknowledgements

Financial supports from the Centre national de la recherche scientifique (CNRS), the University of Bordeaux,

the Université Rennes 1, the Conseil régional d'Aquitaine, GIS Advanced Materials in Aquitaine (COMET Project), the ANR through contract n° ANR-09-BLAN-0175-04 (to R.C.; NT09_469563, AC-MAGnets project) and ANR-09-BLAN-0173-03 (to M. F.) are gratefully acknowledged.

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