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Heterobimetallic structures based on cyano substituted bis-dithiolene complexes and Ni and Cu cyclam cations

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Dedicated to … on the occasion of … *((optional))*

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Five charge transfer salts based on the combination of Fe^{III} and Cu^{II} bisdithiolene anionic complexes containing nitrile groups with $[M(cyclam)]^{2+}$ (M= Ni, Cu) cations; $[Ni(cyclam)]_2[Cu(dcbdt)_2]_2.4DMF$ (**1**), $[Ni(cyclam)]_2[Cu(dcdmp)_2]_2.4DMF$ (**2**), $[Cu(cyclam)]_2[Cu(dcdmp)_2]_2.4DMF$ (**3**), $[Cu(cyclam)]_2[Fe_2(cbdt)_4]_2.4DMF$ (**4**) and $[Nu(cyclam)]_2[Fe_2(cbdt)_4]_2.4DMF$ (**5**) (cbdt=4-cyanobenzene-1,2-dithiolate, dcdmp= 4,5-dicyanobenzene-1,2-dithiolate, dcdmp= 2,3-dicyano-5,6-dimercaptopyrazine) were prepared and characterised namely by X-ray diffraction and magnetisation measurements. The crystal structures of **1-4** were determined by single crystal X-ray diffraction revealing that the cyano groups from dithiolene complexes fail to coordinate the metal ions in cyclam units, which are instead coordinated by solvent molecules or by dithiolene S atoms and cyclam N–H groups participating in hydrogen bonds to the nitrile and sulfur moieties in the anions. This new type of apical M-S coordination provide a path for strong antiferromagnetic interactions, particularly with the nickel cyclam cations.

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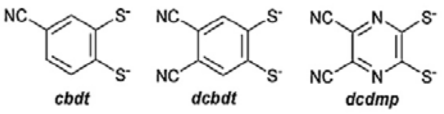
Introduction

Transition metal bisdithiolene complexes have been intensively studied during the last decades,[1] finding important applications particularly significant in different fields such as in biochemistry as biomimetic enzimatic models[2] and in materials science as components for electric and or magnetic materials.[3] The attractive properties of the bisdithiolene complexes result largely from the large contribution of the dithiolene ligands to the frontier orbitals, leading to quite vivid redox behaviour with several stable oxidation states which can have quite different magnetic moments.

Transition metal bisdithiolene complexes bearing nitrogen containing coordinating units have more recently regarded as interesting units for heterometallic magnetic networks. The diversity of magnetic moments of the dithiolene complexes, depending on the metal and oxidation states, can be a priori combined via nitrogen coordination with other paramagnetic ions and several very interesting magnetic networks, where the dithiolene complexes act as bridging coordinating ligands, are expected to be formed.[4] Although several dithiolene substituted with pyridine or pyrazine groups have been recently explored in view of this possibility,[5] the cyano groups present in simpler ligands such as in mnt (mnt=cis-1,2-dicyano-1,2-ethylenedithiolate) may offer a more direct and less complex approach to build heterometallic coordination networks.

Indeed, complexes based on mnt, tfadt, and adt (tfadt = 2-(trifluoromethyl)acrylonitrile-1,2-dithiolate, adt = 2-cyano-1,2-ethanedithiolate) ligands have been previously shown to lead to coordination polymeric structures when combined with metal cyclam[6] crown ethers[7], metalloporphyrines[8] and other metal cations.[9] However the possible preparation of similar compounds based on more extended ligands with cyano groups, has been essentially unexplored. In this paper we describe several compounds resulting from the combination of known Fe^{III} and Cu^{II} bisdithiolene complexes based on cbdt, dcbdt and dcdmp ligands (cbdt=4-cyanobenzene-1,2-dithiolate, dcdmp=4,5-dicyanobenzene-1,2-dithiolate, dcdmp= 2,3-dicyano-5,6-dimercaptopyrazine, see scheme 1) with cations $[M(cyclam)]^{2+}$ (M=Ni, Cu), aiming at obtaining new bimetallic coordination structures, where the nitrile substituents could eventually coordinate the cationic cyclam complexes. In these compounds however, a new coordination between the dithiolene complexes and the metal cyclam ion via the S atoms, is observed, as detailed below.

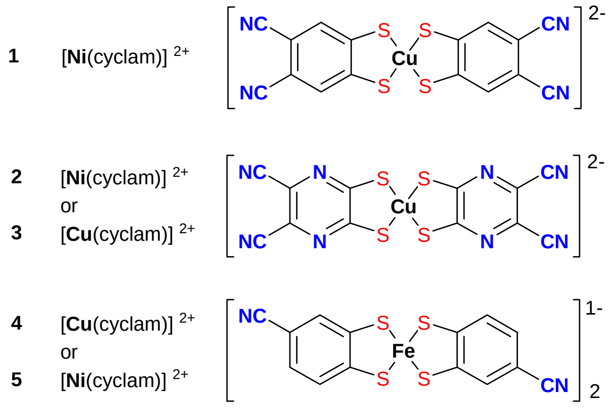


Scheme 1

Results and Discussion

Synthesis

All compounds were prepared under inert atmosphere by metathesis reactions, in which a solution of M(cyclam) in degassed DMF was added to solution of the dithiolene complex in the same solvent. The resulting compounds were obtained as crystalline materials by slow diffusion of ethyl ether into the solvent; the reaction mixture was placed in a Schlenk flask containing degassed ethyl ether and allowed to stand for a few days. Among the twelve different combinations between cationic $[M(cyclam)]^{2+}$ (M = Ni, Cu) and anionic Fe^{III} and Cu^{II} bisdithiolene species, five different salts could be isolated in a crystalline state, as detailed in Scheme 2. Crystals suitable for X-ray diffraction were collected (except for compound **5**). All compounds were characterised by elemental analysis (C, H, N, and S) and IR spectroscopy confirming their purity and composition.



Scheme 2

X-ray diffraction studies

The crystals obtained for compounds **1**, **2**, **3** and **4** enabled the structure determination by X-ray diffraction and their crystallographic data are presented in Table 1. Compounds **1**, **2** and **3** are triclinic, *P*-1, with the bisdithiolene complex central metal located in general positions. Compound **4** is monoclinic, $P2_1/n$, where the anion presents the characteristic dimerisation of Fe(III) bisdithiolene complexes, with an inversion centre between the two Fe atoms.

Compound **1** contains two inequivalent $[Ni(cyclam)]^{2+}$ cations both with the Ni atoms in inversion centres, one $[Cu(dcbdt)_2]^{2-}$ and one DMF molecule, disordered in an inversion centre. The crystal structure consists in almost regular chains of $[Ni(cyclam)]^{2+}$ units alternating with $[Cu(dcbdt)_2]^{2-}$, along *c-a* in a face-to-face arrangement, with the solvent DMF molecules incorporated in the free space of the structure (Figure 1). The intramolecular Cu-S bond distances (Cu-S1 2.2719(7) Å, Cu-S2 2.2755(6) Å, Cu-S3 2.2613(6) Å, Cu-S4 2.2715(6) Å) are typical of dianionic bisdithiolene complexes. However a slight tetrahedral distortion is observed in the $[Cu(dcbdt)_2]^{2-}$ anions, as often observed in Cu dianionic dithiolene complexes,[1] with a dihedral angle of λ=16.98 ° between the two ligands which are essentially planar. In the anion-cation chains (Figure 2), short N–H$\cdots$S hydrogen bonds are identified, with H$\cdots$S distances, at 2.634(3) and 2.725(3) Å with Ni(1) cyclam complex, and at 2.465(3) and 2.624(3) Å with Ni(2) cyclam complex. The Ni-Cu distances in the chains are well above the sum of the Van der Waals radii, with Cu1$\cdots$Ni1* at 4.008 Å (* = 1+x, y, z), and Cu1$\cdots$Ni2* at 4.071 Å (* = x, y, z). Thus, in this first salt, the nitrile does not play any coordination role and the large dicationic and dianionic moieties then stack into alternated chains, held together with N–H$\cdots$S hydrogen bonds.

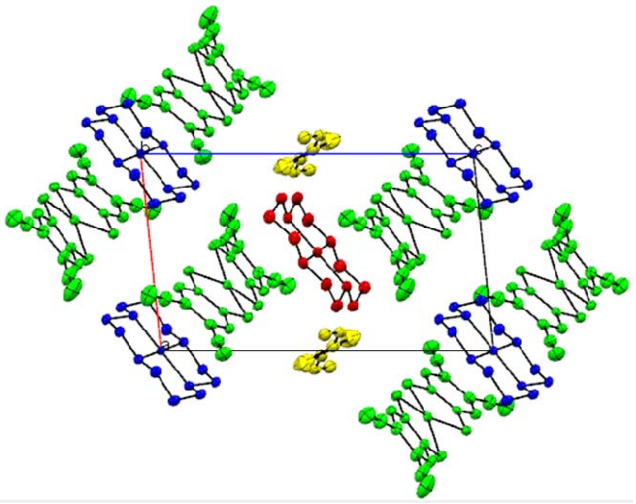


Figure 1. $[Ni(cyclam)]_2[Cu(dcbdt)_2]_2$.DMF (**1**) crystal structure viewed along *b* (hydrogen atoms were omitted for clarity)

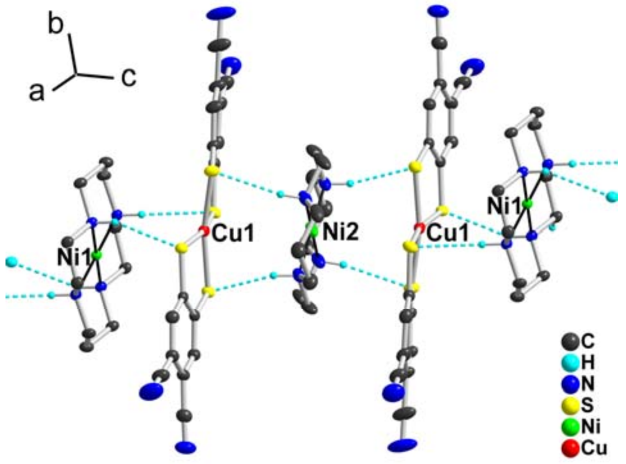


Figure 2. View of the anion-cation chain arrangement in **1**, evidencing the N–H$\cdots$S hydrogen bonds (Hydrogen atoms linked to carbon atoms were omitted for clarity).

Compounds **2** and **3** are isostructural, with two non-equivalent $[M(cyclam)]^{2+}$ cations, both with the metal atoms in inversion centres, one $[Cu(dcdmp)_2]^{2-}$ anion and two DMF molecules in general position. The anions form face to face pairs which are arranged in a 2-D network, in the *a,c* plane, separated by layers of two types of cations: one of the $[M(cyclam)]^{2-}$ (M=Ni, Cu) units has the central metal axially coordinated with two DMF molecules and it is tilted 45° relatively to the *b,c* plane, while the other $[M(cyclam)]^{2-}$ unit is almost parallel to the *a,c* plane, sandwiching the pairs of anions (Figure 3). The central metal M of this second unit, instead of a DMF molecule in the coordination sphere, presents short axial bonds towards one of the dithiolene sulfur atoms (Ni1-S1 3.169 Å in **2** and Cu1-S3 3.082 Å in **3**) (Figure 4). This coordination of the metal cyclam dication by a sulfur atom of the $[Cu(dcdmp)_2]^{2-}$ complex is complemented by additional N–

H···S and N–H···N hydrogen bonds, involving the sulfur atoms of the dithiolene (as in **1**) but also the nitrogen atoms of the pyrazine rings as hydrogen bond acceptors (Figure 4). The $[Cu(dcdmp)_2]^{2-}$ anions in both compounds present intramolecular Cu-S bond distances (on compound **2**: Cu-S1 2.2778(9) Å, Cu-S2 2.2629(9) Å, Cu-S3 2.2570(9) Å, Cu-S4 2.2559(9) Å; on compound **3**: Cu-S1 2.2579(8) Å, Cu-S2 2.2511(7) Å, Cu-S3 2.2867(8) Å, Cu-S4 2.2559(8) Å) typical of dianionic bisdithiolene complexes, and comparable to those of **1** and again a significant tetrahedral distortion is observed in the Cu coordination associated with a dihedral angle between the two dcbdt ligands of 22.93°° for **2** and of 25.48 º for **3**.

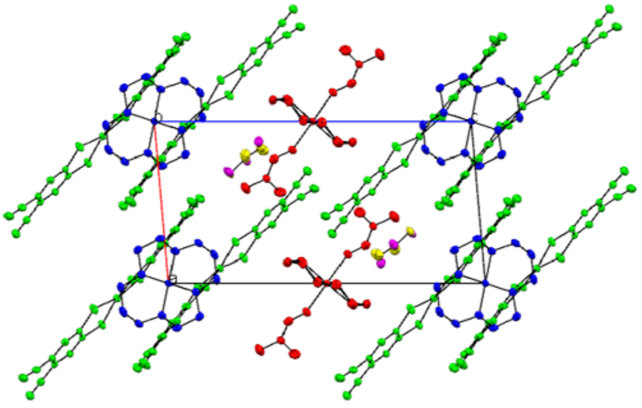


Figure 3. $[Ni(cyclam]_2[Cu(dcdmp)_2]_2$.4DMF (**2**) crystal structure, viewed along *b* (hydrogen atoms were omitted for clarity).

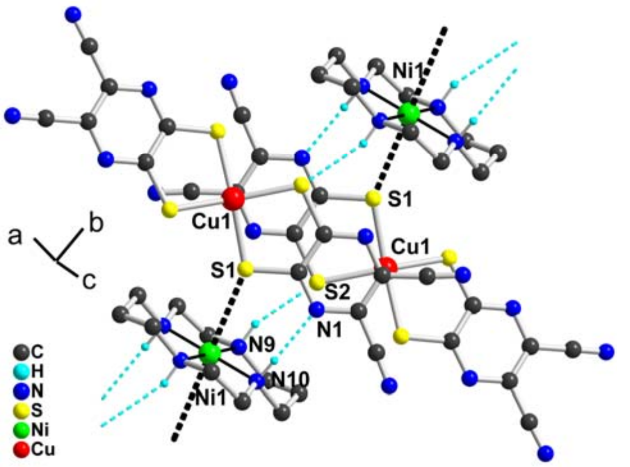


Figure 4. Intermolecular contacts between dianionic and dicationic moieties in $[Ni(cyclam)]_2[Cu(dcdmp)_2]_2$.4DMF (**2**): N–H···S and N–H···N hydrogen bonds as cyan dotted lines, Ni···S coordination as thick black dotted lines (Hydrogen atoms linked to carbon atoms were omitted for clarity). Structural charactetistics of hydrogen for N9–H9···S2: H9···S2: 2.532(4) Å, N9···S2: 3.339(5) Å, N9–H9···S2: 148.0(2)°; for N10–H10···N1: H10···N1: 2.131(3) Å, N10···N1: 3.024(5) Å, N10–H10···N1: 166.8(2)°.

The structure of **4** contains one $[Cu(cyclam)]^{2+}$ with the metal at an inversion centre, apically coordinated by two DMF molecules, a dimerised $[Fe_2(cbdt)_4]^{2-}$ anion with an inversion centre between the Fe atoms and an additional DMF molecule. The crystal structure of **4** consists in an alternated arrangement of anions and cations, typical of ionic compounds with an additional DMF molecule enclosed in the structure, as shown in Figure 5. The geometry of the $[Fe_2(cbdt)_4]^{2-}$ anion is typical of the dimerised Fe(III) bisdithiolene complexes, with basal Fe-S bond distances of Fe-S1 2.2233(18) Å, Fe-S2 2.2095(19) Å, Fe-S3 2.2270(17) Å, Fe-S4 2.2282(18) Å, and two apical Fe-S4A bonds at 2.4849(17) Å, virtually identical to the previously described salt with (n-Bu_4N).[10] The N–H groups of the $[Cu(cyclam)]^{2+}$ complex are also engaged in hydrogen bonds, with the sulfur and CN moieties of neighbouring $[Fe_2(cbdt)_4]^{2-}$ complexes (see Figure S2).

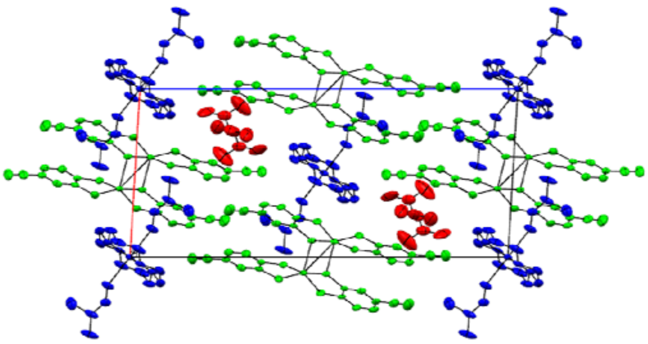


Figure 5. $[Cu(cyclam)]_2[Fe_2(cbdt)_4]_2$.4DMF (**4**) crystal structure, viewed along *b*.

In conclusion, it appears that the enlargement of the dithiolene complexes, where passing from the smaller mnt, adt or tfadt ligands to the larger benzenedithiolate-based cbdt, dcbdt and dcdmp ligands, favours face-to-face organisations, either between cations and anions (in **1**) or between anions (in **2** and **3**), with an associated coordination of the metal cyclam complex in apical position by a sulfur atom of the dithiolene ligand, as observed in **2** and **3**. This unexpected mode of coordination may lead to strong magnetic interactions between paramagnetic species, as detailed below.

Magnetic Properties

As expected, all compounds are paramagnetic and their χ_pT product as determined from experimental magnetisation data after a correction for diamagnetism estimated from tabulated Pascal constants is shown in Figures 6 and 7. The high temperature values for **1**, **2** and **3** correspond to effective magnetic moments of 2.52 μ_B, 3.92 μ_B and 3.50 μ_B respectively. The χ_pT values in the high temperature range are not temperature independent, and upon cooling they decrease slightly for **1** and more significantly for **2**, while slightly increasing for **3**. At lower temperatures, below 40, 70 and 10 K respectively, the χ_pT values start decreasing faster upon cooling, denoting the presence of dominant antiferromagnetic interactions.

EPR spectra of $[Ni(cyclam]_2[Cu(dcbdt)_2]_2$.DMF (**1**) measured in a polycrystalline sample at room temperature presents an asymmetric EPR signal, as shown in figure 8, centered at g = 2.0236 and with width $\Delta H_{pp} = 39.5$ G, which is ascribed to the Cu anions since in the X-band the $S = 1$ signal of Ni is rarely observed due to the zero field splitting. Indeed these values are comparable to those of the $(n\text{-}Bu_4N)_2[Cu(dcbdt)_2]_2$ ($g = 2.045$).[11]

Table 1. Crystallographic data for compounds $[Ni(cyclam)]_2[Cu(dcbdt)_2]_2.4DMF$ **(1)**, $[Ni(cyclam)]_2[Cu(dcdmp)_2]_2.4DMF$ **(2)**, $[Cu(cyclam)]_2[Cu(dcdmp)_2]_2.4DMF$ **(3)** and $[Cu(cyclam)]_2[Fe_2(cbdt)_4]_2.4DMF$ **(4)**.

	(1)	**(2)**	**(3)**	**(4)**
Crystal size (mm)	0.42x0.36x0.14	0.26x0.14x0.07	0.27x0.12x0.09	0.11x0.09x0.03
Crystal Colour and shape	brown prism	brown prism	brown prism	dark red prism
Empirical formula	$C_{55}H_{63}N_{17}Cu_2S_8ONi_2$	$C_{56}H_{76}N_{28}Cu_2S_8O_4Ni_2$	$C_{56}H_{76}N_{28}Cu_4S_8O_4$	$C_{86}H_{100}N_{20}S_{16}O_4Cu_2Fe_4$
Molecular mass	1479.18	1706.37	1716.07	2365.33
Crystal system	triclinic	Triclinic	triclinic	monoclinic
Space group (no.)	*P*-1	*P*-1	*P*-1	$P2_1/n$
Temperature (K)	150(2)	150(2)	150(2)	150(2)
a (Å)	8.7379(9)	9.7846(11)	9.9885(3)	11.5281(9)
b (Å)	13.1327(6)	10.0738(11)	10.0499(2)	9.8161(7)
c (Å)	14.2356(6)	19.052(2)	18.7511(5)	26.511(2)
α (°)	82.934(2)	80.875(5)	80.4800(10)	90.00
β (°)	82.900(2)	83.617(5)	83.4580(10)	93.488(3)
γ (°)	78.269(2)	80.714(4)	80.2180(10)	90.00
V (Å^3)	1579.11(12)	1822.8(4)	1822.24(8)	2994.5(4)
Z, $D_{calcd.}$ (Mg/m^3)	1, 1.556	2, 1.555	2, 1.556	2, 1.474
μ (mm^{-1})	1.570	1.378	1.446	1.162
F(000)	762	882	876	1378
Theta range (°)	1.45 to 27.65	1.09 to 27.54	1.11 to 27.50	1.54 to 27.53
Index range (*h*,*k*,*l*)	-8/11, -17/16, -18/18	-12/12, -10/13, -24/24	-12/12, -12/13, -24/23	-14/14, -12/9, -34/34
Refl. collected	17275	18016	16078	20158
Refl. unique/*R*int	7209/0.0348	7862/0.0362	8199/0.0348	6862/0.0608
Transmission max./min.	0.843/0.604	0.908/0.793	0.878/0.812	0.966/0.882
No. of refined parameters	411	488	488	363
Goodness-of-fit on *F*2	1.092	1.040	1.071	1.118
Final *R*1, [$I > 2\sigma(I)$], *wR*2	0.0317/0.1041	0.0388/0.1380	0.0394/0.1312	0.0747/0.2287

The effective magnetic moment of **1** at 300 K (2.52 μ_B) is much smaller than that expected for two $S = 1$ and two $S = ½$ spins with $g \approx 2$, $\mu_{eff(calc)} = 4.68\ \mu_B$, denoting the presence of strong antiferromagnetic (AFM) interactions between spins in anions and cations. In view of the structure with an almost regular chain of alternating anions and cations closely spaced the magnetic properties are expected in a first approximation to be modelled as a regular chain of alternated $S = 1$ and $S = ½$ spins antiferromagneticaly coupled, which at low temperature is analogous to a regular $S = ½$ spin chain[12]

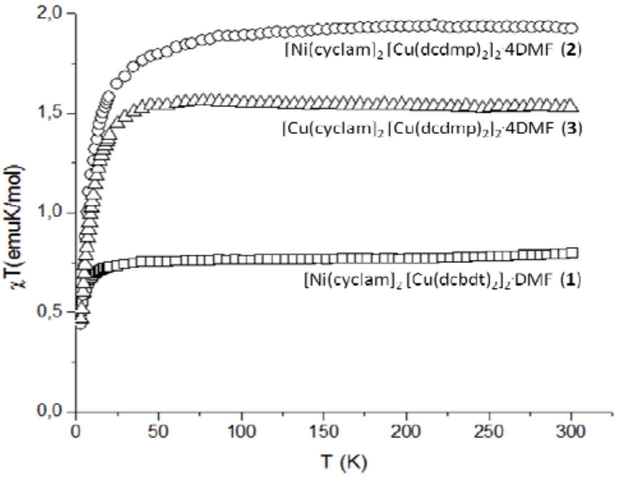


Figure 6. χ_pT as a function of temperature T for compounds **1** (squares), **2**(circles) and **3** (triangles).

$[Ni(cyclam)]_2[Cu(dcdmp)_2]_2.4DMF$ (**2**) is EPR silent. The experimental effective magnetic moment for **2** at 300K is 3.92 μ_B, which is much smaller than 5.05μ_B, expected for two S=1 spins in the Ni(cyclam) cations with with $g \approx 2.26$[13] and two S=1/2 spins in $[Cu(dcdmp)_2]^{2-}$ anions with $g \approx 2{,}03$,[14] denoting the presence of strong AFM interactions between spins which may also explain the absence of any line typical of the $[Cu(dcdmp)_2]$ in the EPR spectra. The dominant AFM interactions in this compound most probably are between the anions and one of the cations, through the original coordination of one of the Ni cyclam cations by two dithiolene sulfur atoms.

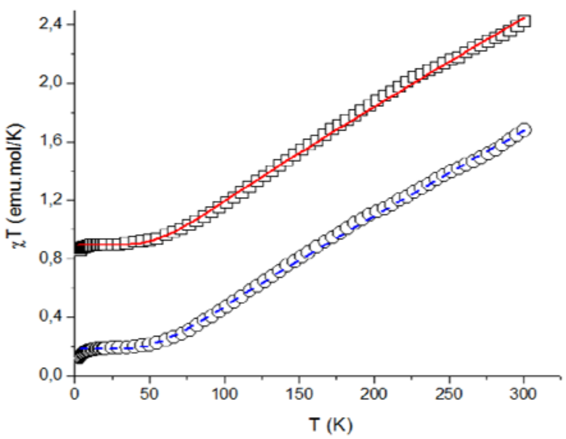


Figure 7. χ_pT as a function of temperature T for compounds. $[Cu(cyclam)]_2[Fe_2(cbdt)_4]_2.4DMF$ **(4)** (circles); and $[Ni(cyclam)]_2[Fe_2(cbdt)_4]_2.4DMF$ **(5)** (squares). The lines are fits with eq 1 (see text).

The EPR spectra of $[Cu(cyclam]_2[Cu(dcdmp)_2]_2.4DMF$ (**3**) as a polycrystalline sample measured at 77° K (Figure 8) shows an asymmetric EPR signal, $g = 2.064$ and $\Delta H_{pp} = 64$ G. The shape of the spectra can be understood as the result of the contributions of cation and anion signals with slightly different parameters.[6a,14] Measurements made on a single crystal shows a complex pattern with up to three lines in the range $g = 2.03\text{-}2.09$ depending on the crystal orientation (Fig. S3).

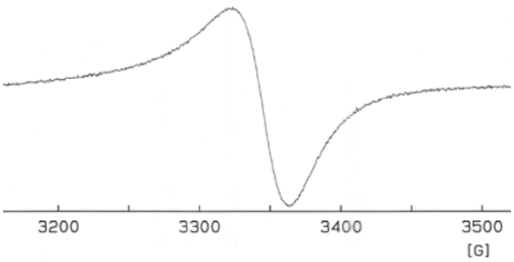


Figure 8. EPR spectra of $[Ni(cyclam]_2[Cu(dcbdt)_2]_2.DMF$ (**1**) as a polycrystalline sample at room temperature.

The experimental effective magnetic moment of $[Cu(cyclam)]_2[Cu(dcdmp)_2]_2.4DMF$ (**3**) is 3.50 μ_B at 300 K, which is close to the calculated value, $\mu_{eff(calc)}$=3.57 μ_B, considering four $S = ½$ with $g = 2.064$. Upon cooling from 300 to 50 K there is a slight increase of the effective magnetic moment, followed by a decrease below 50 K, as previously mentioned, indicating a competition between ferromagnetic and antiferromagnetic interactions, the last ones becoming dominant at low temperatures. Compared with the Ni(cyclam) analogue **2**, the weaker magnetic interactions in **3** might find their origin in the nature of the magnetic orbital involved in both systems. Indeed, in the copper cyclam, the magnetic orbital is essentially a $dx^2\text{-}y^2$ orbital lying in the CuN_4 plane, and thus weakly modified by the apical coordination of the dithiolene complex thought the Cu···S interaction. On the other hand, the Ni(cyclam) complex ($S = 1$) in **2** provides two magnetic orbitals, $dx^2\text{–}y^2$ and dz^2, the latter interacting strongly with the dithiolene complex.

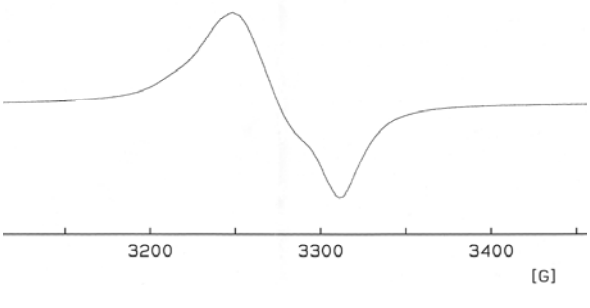


Figure 9: EPR spectra of $[Cu(cyclam]_2[Cu(dcdmp)_2]_2.4DMF$ (**3**) as a polycrystalline sample measured at 77° K.

Compound **5** was found to be EPR silent as expected because both [Ni(cyclam)] cations and the dimerised $[Fe_2(cbdt)_4]_2$ anions generally do not present any observable line in the X-band. The EPR spectra of $[Cu(cyclam)]_2[Fe_2(cbdt)_4]_2.4DMF$ **(4)** as a polycrystalline sample at 77°K, presents one line at $g = 2.068$ and $\Delta H_{pp} =$ 160 G (Figure 9) wide which is ascribed to the $[Cu(cyclam)]^{2+}$ cation.

Although the crystal structure could be solved only for **4**, one may expect that it is isostructural to **5**. In view of the crystal structure of **4**, the magnetic susceptibility of these compounds is expected to result in a first approximation from two almost independent contributions from cations and anions. The anion contribution is expected to follow an antiferromagnetically coupled pair contribution of $S = 3/2$ spins, typical of dimerised Fe bisdithiolene complexes.[10,15]

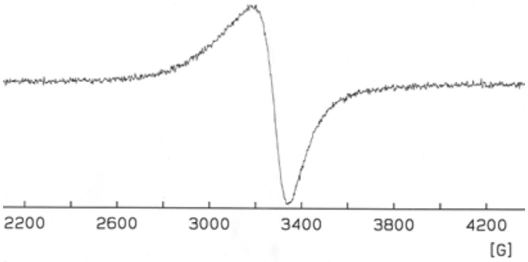


Figure 10: EPR spectra of $[Cu(cyclam)]_2[Fe_2(cbdt)_4]_2.4DMF$ **(4)** as a polycrystalline sample at 77° K.

Therefore, the magnetic susceptibility of **4** and **5** data were tentatively fitted to equation 1, considering, besides a possible temperature independent contribution *A*, a Curie type contribution of the cations and for the anions a contribution of antiferromagnetic coupled $S = 3/2$ dimers (eq 1),

$$\chi_p = A + \frac{C}{T} + \frac{4Ng^2\mu_B{}^2}{kT}\frac{e^{J/kT}+5e^{3J/kT}+14e^{6J/kT}}{1+3e^{J/kT}+5e^{3J/kT}+7e^{6J/kT}} \qquad (1)$$

where *N* is the Avogadro number, *g* is the Landé factor, μ_B is the Bohr magneton and *J* is the intradimer antiferromagnetic coupling parameter and *k* the Boltzmann constant. The values obtained from the fit of this equation to experimental data of **4** and **5** (lines in Figure 7) for $-J/k$ were 256 K and 259 K and for g 1.73 and 1.78 for compounds **4** and **5** respectively, in excellent agreement with those found for $(n\text{-}Bu_4N)_2[Fe(cbdt)_2]_2$, $-J/k$ = 276 K, $g = 1.81$.[10] The Curie constants C obtained for **4** and **5** were 0.187 and 0.895 emu mol/K respectively, which are slightly smaller than those expected for $S = 1$ and $S = 1/2$ units, probably as a result of significant antiferromagnetic interactions.

Conclusions

In summary, a diversity of heterobimetallic coordination structures based on the combination of metal cyclam cations with transition metal bisdithiolene complexes with extended ligands containing cyano groups, have been prepared. While in related salts based on mnt and analogous small ligands, prepared in acetonitrile the cyano groups of the dithiolene ligands coordinate to the metal cyclam, in these extended compounds obtained in DMF, they fail to coordinate to the metal cyclam cations that are instead coordinated by solvent molecules. Besides the competition of DMF solvent molecules with cyano groups from dithiolene complexes towards the coordination of metal ions in cyclam units, as already described in related compounds,6·7[b] a new coordination of the dithiolene towards the metal cyclam is observed via the S atoms. It provides a path for strong magnetic interactions, particularly with the nickel cyclam complex. Of particular note is also the structural role played by the cyclam N–H groups for hydrogen bonding to the nitrile and sulfur moieties of the anionic dithiolene complexes. Analogous complexes with the N,N',N'',N'''-tetramethylcyclam would avoid this interaction and could favour the direct coordination of the M(cyclam) complex with the nitrile substituents of the dithiolene complexes.[16] This route is currently being investigated.

Experimental Section

General: Previously described procedures were employed to prepare (n-$Bu_4N)_2$ [Cu(dcbdt)$_2$],[11] (n-$Bu_4N)_2$ [Cu(dcdmp)$_2$],[14] and (PPh_4)[Fe(cbdt)$_2$].[10] Other starting reagents were obtained commercially and were used as received. Elemental analyses were performed by the analytical services of Instituto Tecnológico e Nuclear using an EA 110 CE Instruments automatic analyser. Melting points were performed on a Stuart Scientific SMP2. IR spectra were recordred with a Varian 640-IR spectrometer in ATR mode.

Synthesis of [Ni(cyclam)]$_2$ [Cu(dcbdt)$_2$]$_2$.DMF (1): A solution of (n-$Bu_4N)_2$ [Cu(dcbdt)$_2$] (0.01 g, 1.08 x 10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of [Ni(cyclam)]($BPh_4)_2$ (0.01 g, 1.08×10^{-5} mol), also in 0.5 mL of degassed DMF. The mixture was filtered to a test tube, which was placed in diethyl ether atmosphere and kept in a dark room. Black needle shaped crystals were collected after five days, washed with dicholoromethane and kept in diethyl ether until they were submitted to X-ray diffraction, 5.3 mg, 3.58 mmol, η = 33%; M.p. > 350°C; IR (ATR) ῦ = 3075 (w, Ar-H), 2221 (m, C≡N), 1558 (m, C=C), 1214-1109 (m, C-N aliphatic) cm^{-1}; $C_{55}H_{63}N_{17}Cu_2S_8ONi_2$; FW=1479.18 g/mol. CNHS (calc)/exp: C (44.66)/45.26; H (4.29)/5.25; N (16.09)/15.40; S (17.34)/16.42

Synthesis of [Ni(cyclam)]$_2$ [Cu(dcdmp)$_2$]$_2$.4DMF (2): A solution of (n-$Bu_4N)_2$ [Cu(dcdmp)$_2$] (0.01 g, 1.07 x 10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of [Ni(cyclam)]($BPh_4)_2$ (0.01 g, 1.07×10^{-5} mol), also in 0.5 mL of degassed DMF. The mixture was filtered to a test tube, which was placed in diethyl ether atmosphere and kept in a dark room. Black needle shaped crystals were collected after five days, washed with dichloromethane and kept in diethyl ether until they were submitted to X-ray diffraction. 4.3 mg, 2.6 mmol, η = 24%; M.p. > 350°C; IR (ATR) ῦ = 2376 (w, -N=C-), 2224 (w, C≡N), 1431-1168 (m-s, pyrazine ring), 728 (w, C-S) cm^{-1}; $C_{56}H_{76}N_{28}Cu_2S_8O_4Ni_2$; FW=1706.37 g/mol. CNHS (calc)/exp: C (39.42)/39.06; H (4.49)/5.15; N (22.98)/23.37; S (15.03)/14.58

Synthesis of [Cu(cyclam)]$_2$[Cu(dcdmp)$_2$]$_2$.4DMF (3): A solution of (n-$Bu_4N)_2$ [Cu(dcdmp)$_2$] (0.01 g, 1.07×10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of [Cu(cyclam)]($BPh_4)_2$ (0.01 g, 1.07×10^{-5} mol), also in 0.5 mL of degassed DMF. The mixture was filtered to a test tube, which was placed in diethyl ether atmosphere and kept in a dark room. Black needle shaped crystals were collected after five days, washed with dichloromethane and kept in diethyl ether until they were submitted to X-ray diffraction. 3.7 mg, 2.2 mmol, η = 21%; M.p. > 350°C; IR (ATR) ῦ = 2360 (w, -N=C-), 2224 (w, C≡N), 1432-1169 (m-s, pyrazine ring), 728 (w, C-S) cm^{-1}; $C_{56}H_{76}N_{28}Cu_4S_8O_4$; FW=1716.07 g/mol. CNHS (calc)/exp: C (39.19)/39.22; H (4.46)/5.36; N (22.85)/22.97; S (14.95)/14.57.

Synthesis of [Cu(cyclam)]$_2$[Fe$_2$(cbdt)$_4$]$_2$.4DMF (4): A solution of (PPh_4)[Fe(cbdt)$_2$] (0.01 g, 1.38×10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of [Cu(cyclam)]($BPh_4)_2$ (0.012 g, 1.38×10^{-5} mol), also in 0.5 mL of degassed DMF. The mixture was filtered to a test tube, which was placed in diethyl ether atmosphere and kept in a dark room. Black needle shaped crystals were collected after five days, washed with dichloromethane and kept in diethyl ether until they were submitted to X-ray diffraction. 1.6 mg, 0.72 mmol, η = 5%; M.p. > 350°C; IR (ATR) ῦ = 3100 (w, Ar-H), 2219 (s, C≡N), 1561-1443 (m-s, C=C), 1102 (s, C-S) cm^{-1}; $C_{86}H_{100}N_{20}$ S_{16} $O_4Cu_2Fe_4$; FW=2365.33 g/mol. CNHS (calc)/exp: C (44.69)/45.61; H (4.26)/4.96; N (11.84)/10.21; S (21.69)/21.44.

Synthesis of [Ni(cyclam)]$_2$ [Fe$_2$(cbdt)$_4$]$_2$.4DMF (5): A solution of (PPh_4)[Fe(cbdt)$_2$] (0.01 g, 1.38×10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of [Ni(cyclam)]($BPh_4)_2$ (0.012 g, 1.38×10^{-5} mol), also in 0.5 mL of degassed DMF. The mixture was filtered to a test tube, which was placed in diethyl ether atmosphere and kept in a dark room. Black needle shaped polycrystals were collected after five days, washed with dichloromethane and diethyl ether. 3.3 mg, 1.4 mmol, η = 11%; M.p. > 350°C; IR (ATR) ῦ = 3120 (w, Ar-H), 2224 (m, C≡N), 1160 (s, C-S) cm^{-1}; $C_{86}H_{100}N_{20}$ S_{16} $O_4Ni_2Fe_4$; FW=2355.64 g/mol. CNHS (calc)/exp: C (44.87)/45.03; H (4.28)/4.33; N (11.89)/10.22; S (21.78)/23.22.

X-ray Crystallographic Study:
Data were collected on a Bruker SMART II diffractometer with single crystals taken in a loop in oil and put directly under the N_2 stream at 150 K. Diffractometer operates with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXS-97, SIR97) [17] and refined (SHELXL-97) by full-matrix least-squares methods,[18] as implemented in the WinGX software package.[19] Absorption corrections were applied. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined, with thermal parameters fixed as 1.2 times U_{eq} of the attached carbon atom. Crystallographic data on X-ray data collections and structure refinements are given Table 1. CCDC-933035-8 contain 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.

EPR Spectroscopy:
EPR spectra at room temperature and 77 K were obtained with a X-band Brucker ESP 300E spectrometer equipped with an ER041XK microwave bridge, a rectangular cavity operating in T102 mode, and ER 032M field controller system. The modulation amplitude was kept well below the linewidth and the microwave power well below saturation.

Magnetic Susceptibility:
Magnetic susceptibility measurements were performed on polycrystalline samples of about 10-20 mg using a 6 Tesla S700X SQUID magnetometer from Cryogenic Ltd. Magnetisation data were obtained in the temperature range 1.7-300 K, under applied magnetic fields up to 1 T. The paramagnetic contributions were obtained from raw magnetisation data after a correction for diamagnetism estimated from tabulated Pascal constants as -7.84, -8.87, -8.85 -12.32 and -12.31×10^{-4} emu/mol for **1** to **5** respectively.

Supporting Information (see footnote on the first page of this article): Figures with structural details of compounds **2**, **3** and **4**, EPR spectra of **3** as a single crystal, and table of selected bond lengths of compounds **1-4**.

Acknowledgments

This work was supported by FCT (Portugal) through contracts PTDC/QUI/64967/2006 and PTDC/QUI-QUI/101788/2008 and by ANR (France) through contract 09-BLAN60175-03. The collaboration between the teams in Portugal and France was also supported by CNRS PICS n° 5760 bilateral action 2011-2013.

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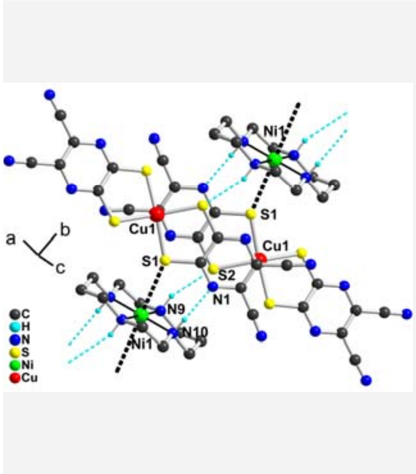
Entry for the Table of Contents

Layout 1:

((Key Topic))

Heterobimetallis structures based on the combination of Fe^{III} and Cu^{II} bisdithiolene anionic complexes containing nitrile groups with $[M(cyclam)]^{2+}$ (M= Ni, Cu) cations, display a new coordination mode of the dithiolene S towards the metal cyclam providing a path for strong magnetic interactions.



A. C. Cerdeira, D. Belo, S. Rabaça, L. C. J. Pereira, J. T. Coutinho, D. Simão, R. T. Henriques, O. Jeannin, M. Fourmigué, M, Almeida,* ……..
Page No. – Page No.

Heterobimetallic structures based on cyano substituted bis-dithiolene complexes and Ni and Cu cyclam cations

Keywords: Heterobimetallic structures / metal-bisdithiolene / metal-cyclam / Magnetic properties

((

Supporting Information

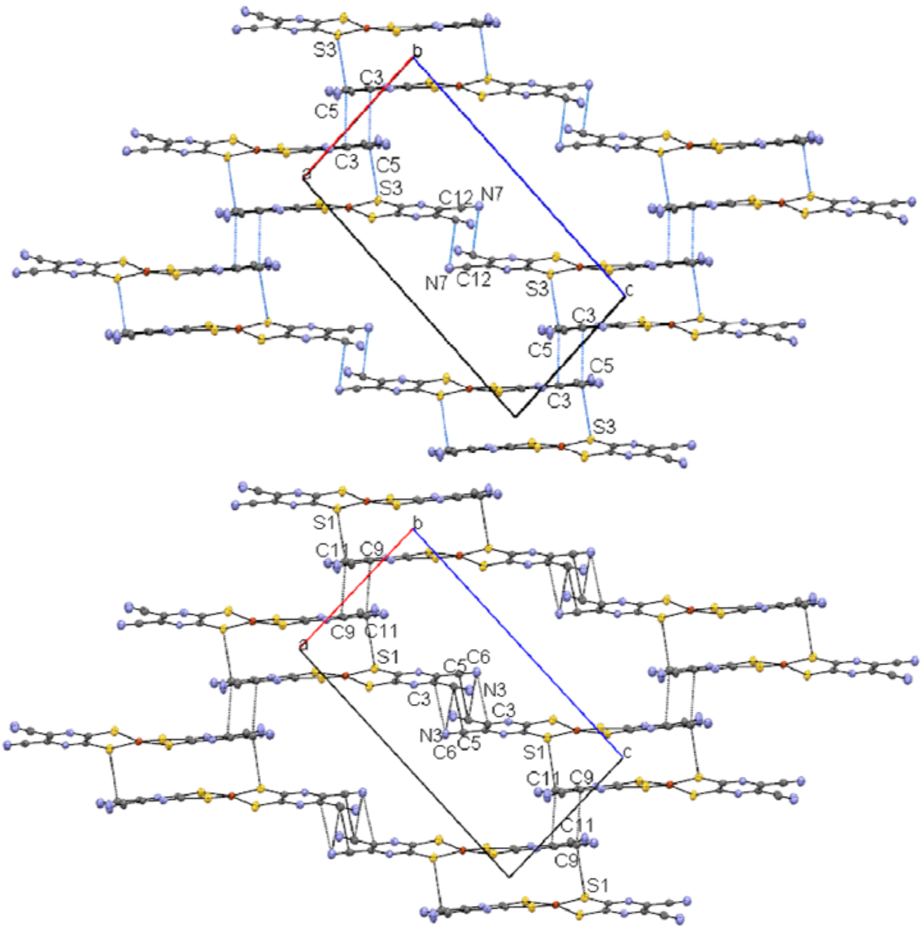


Figure S1. Anionic layers in $[Ni(cyclam)]_2[Cu(dcdmp)_2]_2.4DMF$ (**2**) (top) and $[Cu(cyclam)]_2[Cu(dcdmp)_2]_2.4DMF$ (**3**) (bottom) viewed along *b* emphasising short contacts (hydrogen atoms were omitted for clarity)

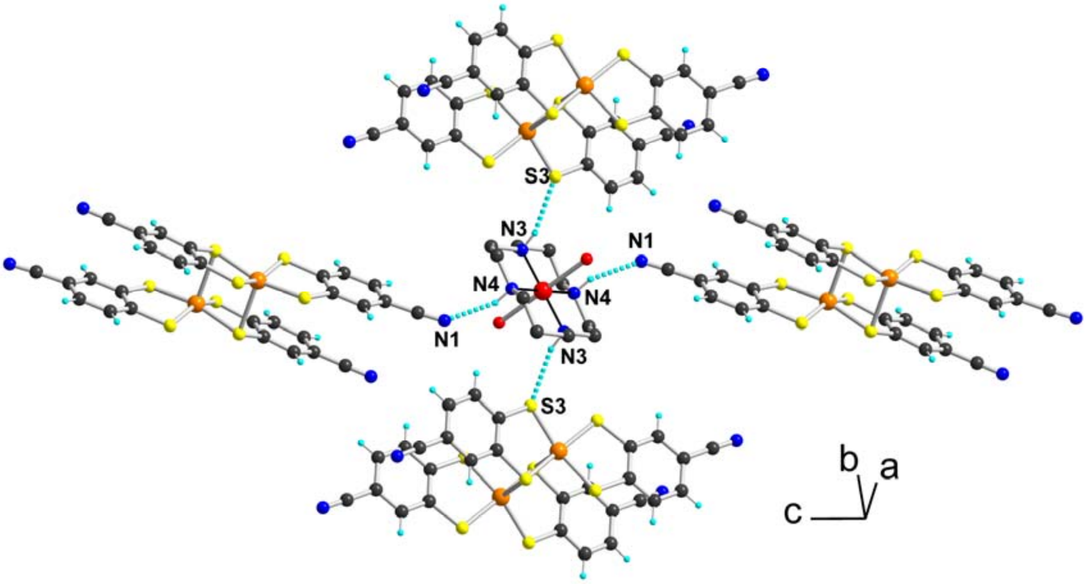


Figure S2. Detail of the hydrogen bond patterns between the N–H moieties of $[Cu(cyclam)]^{2+}$ and the sulfur and nitrile moieties of the bimetallic $[Fe_2(cbdt)_4]^{2-}$ in **4**. The hydrogen atoms on the carbon of the cyclam as well as the DMF molecules coordinating the cyclam have been removed for clarity. Structural characteristics of hydrogen bonds, for N4-H4···N1, H4···N1: 2.322(8), N4···N1: 3.105(10) Å, N4–H4···N1: 143.9(4)°; for N3–H3···S3, H3···S3: 2.552(2), N3···S3: 3.432(6) Å, N3–H3···S3: 162.6(3)°.

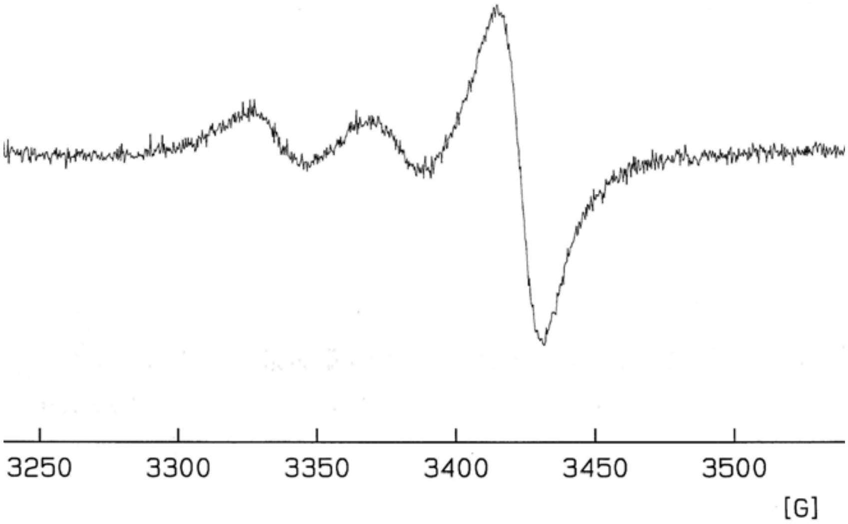


Figure S3. The EPR spectra of $[Cu(cyclam]_2[Cu(dcdmp)_2]_2.4DMF$ (**3**) as a single crystal with H//b at room temperature.

Table S1. Selected bond lengths (Å) for the dithiolene units in compounds **1-4**

	Cu (**1**)	Cu (**2**)	Cu (**3**)	Fe (**4**)
M – S (1)	2.2719(7)	2.2778(9)	2.2579(8)	2.2233(18)
M – S (2)	2.2755(6)	2.2629(9)	2.2511(7)	2.2095(19)
M – S (3)	2.2613(6)	2.2570(9)	2.2867(8)	2.2270(17)
M – S (4)	2.2715(6)	2.2559(9)	2.2559(8)	2.2282(18)
M – S (4A)				2.4849(17)
S (1) – C (1)	1.753(2)	1.722(3)	1.720(3)	1.753(7)
S (2) – C (2)	1.757(2)	1.723(3)	1.718(3)	1.760(7)
S (3) – C (7)	1.753(2)	1.724(3)	1.730(3)	1.752(7)
S (4) – C (8)	1.752(2)	1.716(3)	1.719(3)	1.772(6)
C (1) – C (2)	1.412(3)	1.456(4)	1.453(4)	1.386(9)
C (7) – C (8)	1.411(3)	1.446(4)	1.453(4)	1.384(9)