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Heterodimetallic Structures Based on Cyano-Substituted Bis(dithiolene) Complexes and Ni and Cu Cyclam Cations

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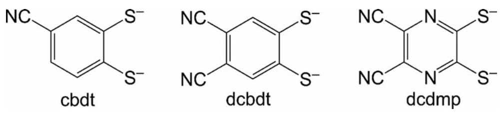
Five charge-transfer salts based on the combination of anionic Fe^{III} and Cu^{II} bis(dithiolene) complexes containing nitrile groups with [M(cyclam)]$^{2+}$ (M = Ni, Cu) cations, namely, [Ni(cyclam)]$_2$[Cu(dcbdt)$_2$]$_2$·4DMF (**1**, dcbdt = 4,5-dicyanobenzene-1,2-dithiolate, DMF = *N*,*N*-dimethylformamide), [Ni(cyclam)]$_2$[Cu(dcdmp)$_2$]$_2$·4DMF (**2**, dcdmp = 2,3-dicyano-5,6-dimercaptopyrazine), [Cu(cyclam)]$_2$[Cu(dcdmp)$_2$]$_2$·4DMF (**3**), [Cu(cyclam)]$_2$[Fe$_2$(cbdt)$_4$]$_2$·4DMF (**4**, cbdt = 4-cyanobenzene-1,2-dithiolate) and [Ni(cyclam)]$_2$[Fe$_2$(cbdt)$_4$]$_2$·4DMF (**5**), were prepared and characterised by X-ray diffraction and magnetisation measurements. The crystal structures of **1**–**4** were determined by single-crystal X-ray diffraction, which revealed that the cyano groups from dithiolene complexes fail to coordinate the metal ions in the cyclam units. Instead, they are coordinated by solvent molecules or by dithiolene S atoms and cyclam N–H groups, which participate in hydrogen bonds to the nitrile and sulfur moieties in the anions.

Introduction

Transition metal bis(dithiolene) complexes have been studied intensively during recent decades[1] and have important applications in different fields such as in biochemistry as biomimetic enzymatic models[2] and in materials science as components for electric and magnetic materials.[3] The attractive properties of the bis(dithiolene) complexes result largely from the large contribution of the dithiolene ligands to the frontier orbitals, which leads to distinct redox behaviour with several stable oxidation states with different magnetic moments.

More recently, transition metal bis(dithiolene) complexes bearing nitrogen-containing coordinating units have been regarded as interesting units for heterometallic magnetic networks. The diversity of the magnetic moments of the dithiolene complexes, which depend on the metal centre and the oxidation states, can be a priori combined with other paramagnetic ions through nitrogen coordination, and several very interesting magnetic networks, in which the dithiolene complexes act as bridging coordinating ligands, are expected to form.[4] Although several dithiolene ligands substituted with pyridine or pyrazine groups have recently been 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 the construction of heterometallic coordination networks.

Indeed, complexes based on mnt, tfadt, and adt [tfadt = 2-(trifluoromethyl)acrylonitrile-1,2-dithiolate, adt = 2-cyano-1,2-ethylenedithiolate] ligands lead to polymeric coordination structures when combined with metal cyclam,[6] crown ethers,[7] metalloporphyrins[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} bis(dithiolene) complexes based on cbdt, dcbdt, and dcdmp ligands (cbdt = 4-cyanobenzene-1,2-dithiolate, dcbdt = 4,5-dicyanobenzene-1,2-dithiolate, dcdmp = 2,3-dicyano-5,6-dimercaptopyrazine, see Scheme 1) with [M(cyclam)]$^{2+}$ cations (M = Ni, Cu) to obtain new dimetallic coordination structures, in which the



Scheme 1.

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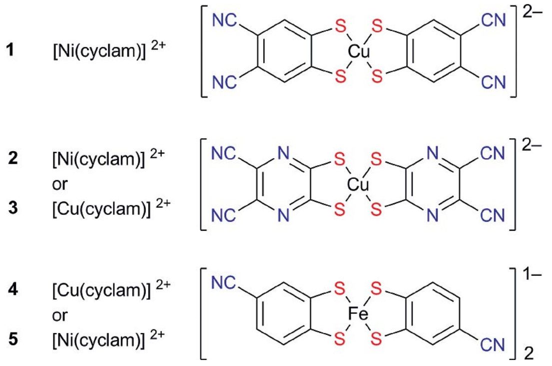
nitrile substituents could coordinate the cationic cyclam complexes.

Results and Discussion

Synthesis

All compounds were prepared under an inert gas by metathesis reactions, in which a solution of [M(cyclam)]$(BPh_4)_2$ in degassed *N*,*N*-dimethylformamide (DMF) was added to a solution of the dithiolene complex in the same solvent. The resulting compounds were obtained as crystalline materials by slow diffusion of diethyl ether into the solution; the reaction mixture was placed in a Schlenk flask containing degassed diethyl ether and allowed to stand for a few days. Of the twelve different combinations of cationic $[M(cyclam)]^{2+}$ (M = Ni, Cu) and anionic Fe^{III} and Cu^{II} bis(dithiolene) species, five different salts could be isolated in a crystalline state, as detailed in Scheme 2, and 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 to confirm their purity and composition.



Scheme 2.

X-ray Diffraction Studies

The crystals obtained for **1**, **2**, **3** and **4** enabled determination of their structures by X-ray diffraction, and their crystallographic data are presented in Table 1. Compounds **1**, **2** and **3** are triclinic, $P\bar{1}$, with the metal centres of the bis(dithiolene) complexes located in general positions. Compound **4** is monoclinic, $P2_1/n$, and the anion presents the characteristic dimerisation of Fe^{III} bis(dithiolene) complexes with an inversion centre between the two Fe atoms.

Compound **1** contains two nonequivalent $[Ni(cyclam)]^{2+}$ cations with the Ni atoms on inversion centres, one $[Cu(dcbdt)_2]^{2-}$ unit and one DMF molecule, which is disordered over an inversion centre. The crystal structure comprises almost regular chains of $[Ni(cyclam)]^{2+}$ units alternating with $[Cu(dcbdt)_2]^{2-}$ units along *c*–*a* in a face-to-face arrangement, and the solvent DMF molecules are incorporated in the free space of the structure (Figure 1). The intramolecular Cu–S bond lengths [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 bis(dithiolene) complexes. However, a slight tetrahedral distortion is observed in the $[Cu(dcbdt)_2]^{2-}$ anions, as is often observed in dianionic Cu dithiolene complexes,[1] and the dihedral angle λ is 16.98° between the two ligands, which are essentially planar. In the anion–cation chains (Figure 2), short N–H···S hydrogen bonds are identified with H···S distances of 2.634(3) and 2.725(3) Å

Table 1. Crystallographic data for **1**–**4**.

	1	**2**	**3**	**4**
Crystal size [mm]	0.42 × 0.36 × 0.14	0.26 × 0.14 × 0.07	0.27 × 0.12 × 0.09	0.11 × 0.09 × 0.03
Crystal colour and shape	brown prism	brown prism	brown prism	dark red prism
Empirical formula	$C_{55}H_{63}Cu_2N_{17}Ni_2OS_8$	$C_{56}H_{76}Cu_2N_{28}Ni_2O_4S_8$	$C_{56}H_{76}Cu_4N_{28}O_4S_8$	$C_{86}H_{100}Cu_2Fe_4N_{20}O_4S_{16}$
Molecular mass	1479.18	1706.37	1716.07	2365.33
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
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
β [°]	82.900(2)	83.617(5)	83.4580(10)	93.488(3)
γ [°]	78.269(2)	80.714(4)	80.2180(10)	90
V [Å^3]	1579.11(12)	1822.8(4)	1822.24(8)	2994.5(4)
Z	1	2	2	2
$D_{calcd.}$ [Mg m^{-3}]	1.556	1.555	1.556	1.474
μ [mm^{-1}]	1.570	1.378	1.446	1.162
F(000)	762	882	876	1378
θ range [°]	1.45–27.65	1.09–27.54	1.11–27.50	1.54–27.53
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
Reflections collected	17275	18016	16078	20158
Unique reflections/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

to the Ni(1) cyclam complex and 2.465(3) and 2.624(3) Å to the Ni(2) cyclam complex. The Ni–Cu distances in the chains are well above the sum of the van der Waals radii; the Cu1···Ni1* distance is 4.008 Å (* = 1 + *x*, *y*, *z*), and the Cu1···Ni2* distance is 4.071 Å (* = *x*, *y*, *z*). Thus, in this first salt, the nitrile groups do not play any coordination role, and the large dicationic and dianionic moieties then stack into alternate chains held together with N–H···S hydrogen bonds.

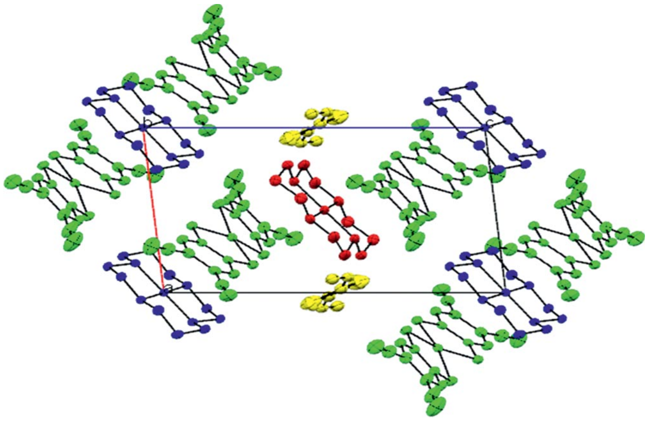


Figure 1. Crystal structure of **1** viewed along the *b* axis (hydrogen atoms omitted for clarity).

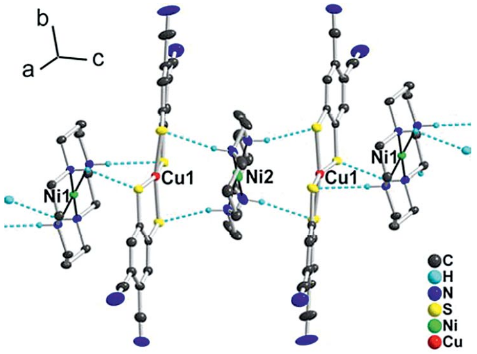


Figure 2. View of the anion–cation chain arrangement in **1** showing the N–H···S hydrogen bonds (hydrogen atoms linked to carbon atoms omitted for clarity).

Compounds **2** and **3** are isostructural and have two nonequivalent [M(cyclam)]$^{2+}$ cations, both with the metal atoms on inversion centres, one [Cu(dcdmp)$_2$]$^{2-}$ anion and two DMF molecules in general positions. The anions form face-to-face pairs, which are arranged in a 2D 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 atom axially coordinated with two DMF molecules and is tilted 45° relatively to the *b*–*c* plane, whereas the other [M(cyclam)]$^{2+}$ unit is almost parallel to the *a*–*c* plane and sandwiches the pairs of anions (Figure 3). Instead of a DMF molecule in the coordination sphere, the central metal atom of this second unit presents short axial contacts towards one of the dithiolene sulfur atoms (Ni1–S1 3.169 Å in **2** and Cu1–S3 3.082 Å in **3**; Figure 4). These short contacts denote a semicoordination of the metal cyclam dication by a sulfur atom of the [Cu(dcdmp)$_2$]$^{2-}$ complex. In addition, there are N–H···S and N–H···N hydrogen bonds with the sulfur atoms of the dithiolene ligands (as in **1**) and 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 lengths [**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; **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 bis(dithiolene) complexes and comparable to those of **1**, and again a significant tetrahedral distortion is observed in the Cu coordination associated with dihedral angles between the two dcbdt ligands of 22.93° for **2** and of 25.48° for **3**.

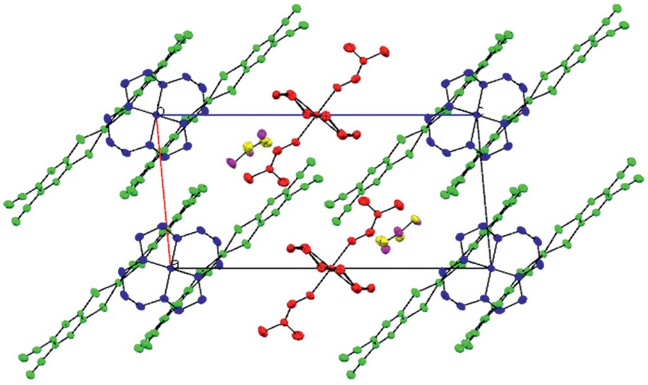


Figure 3. Crystal structure of **2** viewed along the *b* axis (hydrogen atoms omitted for clarity).

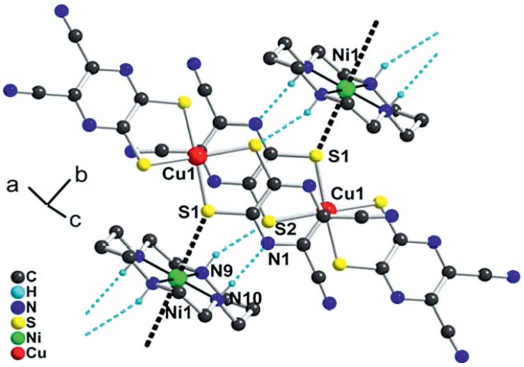


Figure 4. Intermolecular contacts between dianionic and dicationic moieties in **2**: N–H···S and N–H···N hydrogen bonds as cyan dotted lines, Ni···S coordination is shown by thick black dotted lines (hydrogen atoms linked to carbon atoms omitted for clarity). Structural characteristics of hydrogen bonds: N9–H9···S2: H9···S2 2.532(4) Å, N9···S2 3.339(5) Å, N9–H9···S2 148.0(2)°; 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)]$^{2+}$ unit with the metal atom on an inversion centre and 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** has an alternate 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 dimerised Fe^{III} bis(dithiolene) complexes, and the basal Fe–S bond lengths are 2.2233(18), 2.2095(19), 2.2270(17) and 2.2282(18) Å for S1–S4, respectively; the two apical Fe–S4A bond lengths of 2.4849(17) Å are virtually identical to those of the previously described salt with $(nBu_4N)^+$.[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).

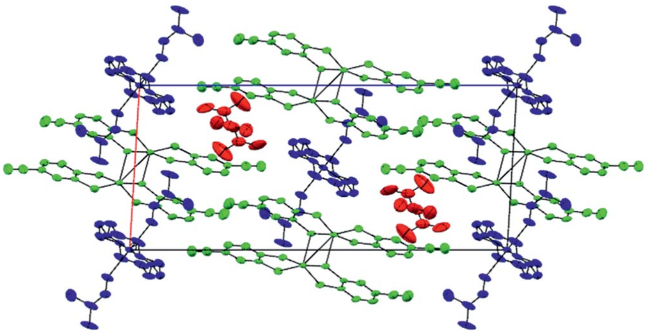


Figure 5. Crystal structure of **4** viewed along the *b* axis.

In conclusion, it appears that the enlargement of the dithiolene complexes from those with the smaller mnt, adt or tfadt ligands to those with 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 apical position of the metal cyclam complex by a sulfur atom of the dithiolene ligand, as observed in **2** and **3**. This unexpected coordination mode 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 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, 3.92 and 3.50 μ_B, respectively. In these compounds, the Cu dianions have $S = 1/2$, and the magnetic moment associated with the Ni cyclam cations depends on their coordination geometry. For a square-planar coordination geometry, they are expected to have a diamagnetic $S = 0$ ground state, whereas for octahedral coordination, an $S = 1$ state is expected. 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**, whereas they slightly increase for **3**. At lower temperatures, below 40, 70 and 10 K respectively, the χ_pT values decrease more rapidly upon cooling, which denotes the presence of dominant antiferromagnetic (AFM) interactions.

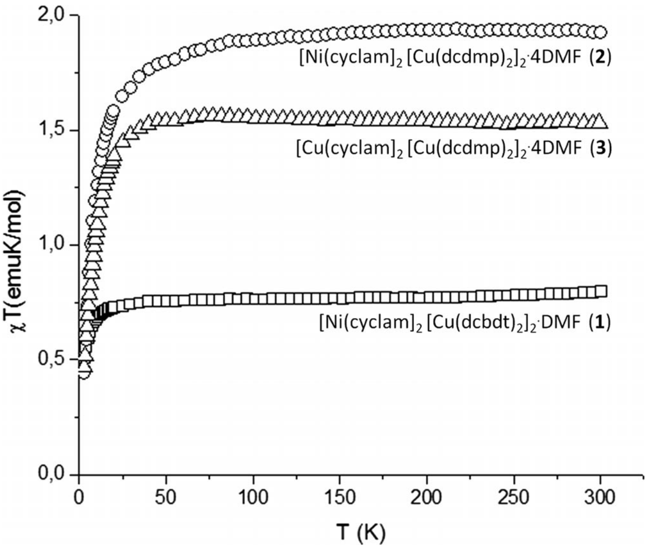


Figure 6. χ_pT as a function of T for **1** (squares), **2** (circles) and **3** (triangles).

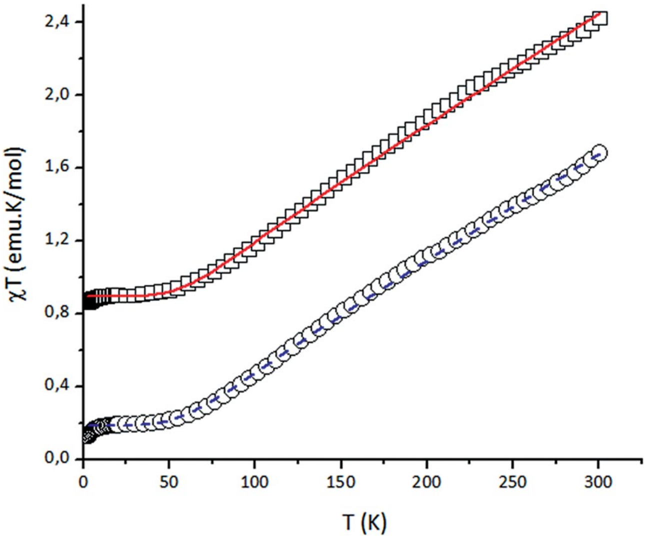


Figure 7. χ_pT as a function of temperature T for **4** (circles) and **5** (squares). The lines are fits with Equation 1 (see text).

The electron paramagnetic resonance (EPR) spectrum of **1** measured for a polycrystalline sample at room temperature presents an asymmetric EPR signal, as shown in Figure 8. The peak is centred at $g = 2.0236$ with width $\Delta H_{pp} = 39.5$ G, which is ascribed to the Cu anions, as the cations are expected to be diamagnetic in view of the square-planar Ni coordination. Indeed, these values are comparable to those of $(nBu_4N)_2[Cu(dcbdt)_2]$ ($g = 2.045$).[11]

The effective magnetic moment of **1** at 300 K (2.52 μ_B) is close to that expected for two $S = 1/2$ (Cu) spins with $g = 2.0236$, $\mu_{eff(calcd.)} = 2.48\ \mu_B$ and denotes rather weak interactions between the spins in the anions that are separated by diamagnetic Ni cations.

$[Ni(cyclam)]_2[Cu(dcdmp)_2]_2{\cdot}4DMF$ (**2**) is EPR-silent. In this compound, one of the Ni cations essentially has a square-planar coordination geometry and is expected to be

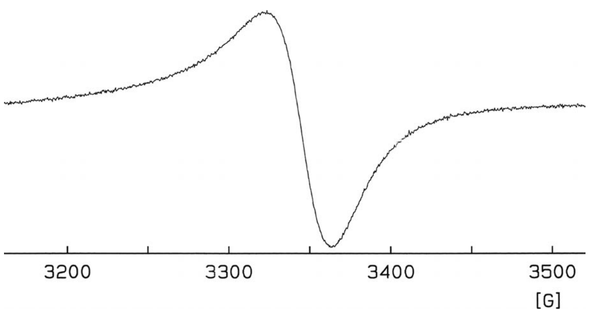


Figure 8. EPR spectrum of polycrystalline **1** at room temperature.

diamagnetic in spite of the long apical S···Ni semicoordinating bonds, whereas the other Ni cation has a clear octahedral coordination geometry and is, therefore, expected to be paramagnetic; however, in the X-band EPR spectrum, the $S = 1$ signal of Ni is rarely observed owing to zero-field splitting. The experimental effective magnetic moment for **2** at 300 K is 3.92 μ_B, which is close to 4.05 μ_B expected for one $S = 1$ spin in the Ni(cyclam) cations with octahedral coordination and $g \approx 2.26$,[12] and two $S = 1/2$ spins in $[Cu(dcdmp)_2]^{2-}$ anions with $g \approx 2.03$.[13] The temperature dependence of the χ_pT product presents a slight decrease upon cooling, which denotes the presence of dominant AFM interactions between spins.

The EPR spectrum of a polycrystalline sample of $[Cu(cyclam)]_2[Cu(dcdmp)_2]_2·4DMF$ (**3**) measured at 77 K (Figure 9) shows an asymmetric EPR signal with $g = 2.064$ and $\Delta H_{pp} = 64$ G. The shape of the spectrum 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 show a complex pattern with up to three lines in the range $g = 2.03–2.09$ depending on the crystal orientation (Figure S3).

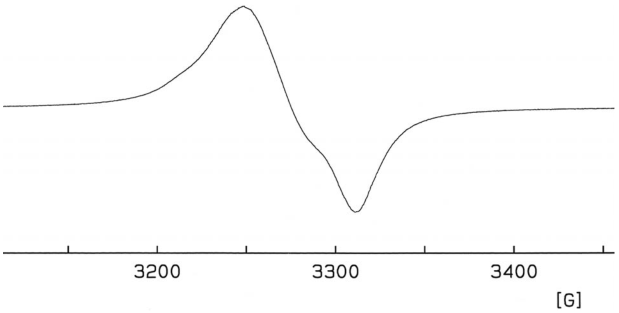


Figure 9. EPR spectrum of polycrystalline **3** at 77 K.

The experimental effective magnetic moment of **3** is 3.50 μ_B at 300 K, which is close to the calculated value of $\mu_{eff(calc)} = 3.57\ \mu_B$ for four $S = 1/2$ spins 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, which indicates competition between ferromagnetic and antiferromagnetic interactions; the latter become dominant at low temperatures.

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 X-band EPR lines. The EPR spectrum of polycrystalline **4** at 77 K (Figure 10) presents one line at $g = 2.068$ and $\Delta H_{pp} = 160$ G, which is ascribed to the $[Cu(cyclam)]^{2+}$ cation.

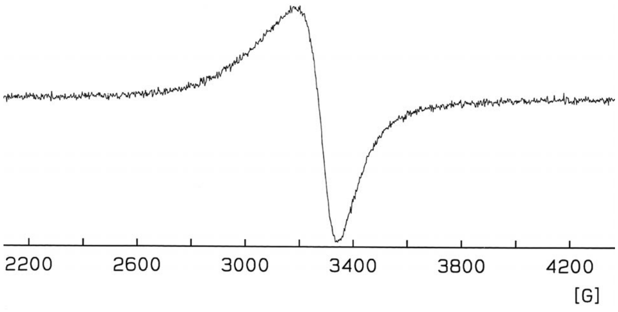


Figure 10. EPR spectrum of polycrystalline **4** at 77 K.

Although the crystal structure of **5** could not be solved, one may expect that it is isostructural to **4**. In view of the crystal structure of **4**, as a first approximation, the magnetic susceptibility of these compounds is expected to result from two almost independent contributions from the cations and anions. The anion contribution is expected to follow the contribution of an antiferromagnetically coupled pair of $S = 3/2$ spins, typical of dimerised Fe bis(dithiolene) complexes.[10,14]

Therefore, the magnetic susceptibility data of **4** and **5** were tentatively fitted to Equation (1), by considering a Curie-type contribution of the cations, a contribution from antiferromagnetically coupled $S = 3/2$ dimers for the anions, in addition to a possible temperature-independent contribution A:

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

in which N is the Avogadro number, g is the Landé factor, μ_B is the Bohr magneton, J is the intradimer antiferromagnetic coupling parameter, and k is the Boltzmann constant. The values obtained from the fit of this equation to the experimental data of **4** and **5** (lines in Figure 7) for $-J/k$ were 256 and 259 K and $g = 1.73$ and 1.78 for **4** and **5**, respectively, in excellent agreement with those found for $(nBu_4N)_2[Fe(cbdt)_2]_2$, $-J/k = 276$ K, $g = 1.81$.[10] The Curie constants C obtained for **4** and **5** of 0.187 and 0.895 emu mol K^{-1}, respectively, are slightly smaller than those expected for $S = 1$ and $S = 1/2$ units, probably as a result of significant antiferromagnetic interactions.

Conclusions

Diverse heterodimetallic coordination structures based on the combination of metal cyclam cations with transition metal bis(dithiolene) complexes with extended ligands containing cyano groups have been prepared. Although the cyano groups of the dithiolene ligands coordinate to the metal cyclam in related salts based on mnt and analogous small ligands prepared in acetonitrile, in these extended compounds obtained in DMF, they fail to coordinate to the metal cyclam cations, which are instead coordinated by solvent molecules. In addition to the competition of DMF solvent molecules with cyano groups from dithiolene complexes for the coordination of metal ions in cyclam units, as already described in related compounds,[6,7] a new secondary coordination of the dithiolene ligand towards the metal cyclam through the S atoms is observed. Of particular note is 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.[15] This route is currently being investigated.

Experimental Section

General: Previously described procedures were employed to prepare $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Cu(dcbdt)}_2]$,[11] $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Cu(dcdmp)}_2]$[14] and $(\mathrm{PPh}_4)[\mathrm{Fe(cbdt)}_2]$.[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 by using an EA 110 CE Instruments automatic analyser. Melting points were measured with a Stuart Scientific SMP2 instrument. IR spectra were recorded with a Varian 640-IR spectrometer in attenuated total reflectance (ATR) mode.

$[\mathrm{Ni(cyclam)}]_2[\mathrm{Cu(dcbdt)}_2]_2\cdot\mathrm{DMF}$ (1): A solution of $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Cu(dcbdt)}_2]$ (0.01 g, 1.08×10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of $[\mathrm{Ni(cyclam)}](\mathrm{BPh}_4)_2$ (0.01 g, 1.08×10^{-5} mol), also in degassed DMF (0.5 mL). The mixture was filtered into a test tube, which was placed in a diethyl ether atmosphere and kept in a dark room. Black needle-shaped crystals were collected after 5 d, washed with dichloromethane and kept in diethyl ether until they were submitted to X-ray diffraction. Yield 5.3 mg, 3.58 mmol, 33%. M.p. >350 °C. IR (ATR): $\tilde{\nu}$ = 3075 (w, Ar–H), 2221 (m, C≡N), 1558 (m, C=C), 1214–1109 (m, C–N aliphatic) cm^{-1}. $\mathrm{C}_{55}\mathrm{H}_{63}\mathrm{Cu}_2\mathrm{N}_{17}\mathrm{Ni}_2\mathrm{OS}_8$ (1479.18): calcd. C 44.66, H 4.29, N 16.09, S 17.34; found C 45.26, H 5.25, N 15.40, S 16.42.

$[\mathrm{Ni(cyclam)}]_2[\mathrm{Cu(dcdmp)}_2]_2\cdot4\mathrm{DMF}$ (2): A solution of $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Cu(dcdmp)}_2]$ (0.01 g, 1.07×10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of $[\mathrm{Ni(cyclam)}](\mathrm{BPh}_4)_2$ (0.01 g, 1.07×10^{-5} mol), also in degassed DMF (0.5 mL). The mixture was filtered into a test tube, which was placed in a diethyl ether atmosphere and kept in a dark room. Black needle-shaped crystals were collected after 5 d, washed with dichloromethane and kept in diethyl ether until they were submitted to X-ray diffraction. Yield 4.3 mg, 2.6 mmol, 24%. M.p. >350 °C. IR (ATR): $\tilde{\nu}$ = 2376 (w, –N=C–), 2224 (w, C≡N), 1431–1168 (m–s, pyrazine ring), 728 (w, C–S) cm^{-1}. $\mathrm{C}_{56}\mathrm{H}_{76}\mathrm{Cu}_2\mathrm{N}_{28}\mathrm{Ni}_2\mathrm{O}_4\mathrm{S}_8$ (1706.37): calcd. C 39.42, H 4.49, N 22.98, S 15.03; found 39.06, H 5.15, N 23.37, S 14.58.

$[\mathrm{Cu(cyclam)}]_2[\mathrm{Cu(dcdmp)}_2]_2\cdot4\mathrm{DMF}$ (3): A solution of $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Cu(dcdmp)}_2]$ (0.01 g, 1.07×10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of $[\mathrm{Cu(cyclam)}](\mathrm{BPh}_4)_2$ (0.01 g, 1.07×10^{-5} mol), also in degassed DMF (0.5 mL). The mixture was filtered into a test tube, which was placed in a diethyl ether atmosphere and kept in a dark room. Black needle-shaped crystals were collected after 5 d, washed with dichloromethane and kept in diethyl ether until they were submitted to X-ray diffraction. Yield 3.7 mg, 2.2 mmol, 21%. M.p. >350 °C. IR (ATR): $\tilde{\nu}$ = 2360 (w, –N=C–), 2224 (w, C≡N), 1432–1169 (m–s, pyrazine ring), 728 (w, C–S) cm^{-1}. $\mathrm{C}_{56}\mathrm{H}_{76}\mathrm{Cu}_4\mathrm{N}_{28}\mathrm{O}_4\mathrm{S}_8$ (1716.07): calcd. C 39.19, H 4.46, N 22.85, S 14.95; found C 39.22, H 5.36, N 22.97, S 14.57.

$[\mathrm{Cu(cyclam)}]_2[\mathrm{Fe}_2(\mathrm{cbdt})_4]_2\cdot4\mathrm{DMF}$ (4): A solution of $(\mathrm{PPh}_4)[\mathrm{Fe(cbdt)}_2]$ (0.01 g, 1.38×10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of $[\mathrm{Cu(cyclam)}](\mathrm{BPh}_4)_2$ (0.012 g, 1.38×10^{-5} mol), also in degassed DMF (0.5 mL). The mixture was filtered into a test tube, which was placed in a diethyl ether atmosphere and kept in a dark room. Black needle-shaped crystals were collected after 5 d, washed with dichloromethane and kept in diethyl ether until they were submitted to X-ray diffraction. Yield 1.6 mg, 0.72 mmol, 5%. M.p. >350 °C. IR (ATR): $\tilde{\nu}$ = 3100 (w, Ar–H), 2219 (s, C≡N), 1561–1443 (m–s, C=C), 1102 (s, C–S) cm^{-1}. $\mathrm{C}_{86}\mathrm{H}_{100}\mathrm{Cu}_2\mathrm{Fe}_4\mathrm{N}_{20}\mathrm{O}_4\mathrm{S}_{16}$ (2365.33): calcd. C 44.69, H 4.26, N 11.84, S 21.69; found C 45.61, H 4.96, N 10.21, S 21.44.

$[\mathrm{Ni(cyclam)}]_2[\mathrm{Fe}_2(\mathrm{cbdt})_4]_2\cdot4\mathrm{DMF}$ (5): A solution of $(\mathrm{PPh}_4)[\mathrm{Fe(cbdt)}_2]$ (0.01 g, 1.38×10^{-5} mol) in degassed DMF (0.5 mL) was added to a solution of $[\mathrm{Ni(cyclam)}](\mathrm{BPh}_4)_2$ (0.012 g, 1.38×10^{-5} mol), also in degassed DMF (0.5 mL). The mixture was filtered into a test tube, which was placed in a diethyl ether atmosphere and kept in a dark room. Black needle-shaped polycrystals were collected after 5 d and washed with dichloromethane and diethyl ether. Yield 3.3 mg, 1.4 mmol, 11%. M.p. >350 °C. IR (ATR): $\tilde{\nu}$ = 3120 (w, Ar–H), 2224 (m, C≡N), 1160 (s, C–S) cm^{-1}. $\mathrm{C}_{86}\mathrm{H}_{100}\mathrm{Fe}_4\mathrm{N}_{20}\mathrm{Ni}_2\mathrm{O}_4\mathrm{S}_{16}$ (2355.64): calcd. C 44.87, H 4.28, N 11.89, S 21.78; found C 45.03, H 4.33, N 10.22, S 23.22.

X-ray Crystallographic Study: Data were collected with a Bruker SMART II diffractometer with single crystals taken in a loop in oil and placed directly under the N_2 stream at 150 K. The diffractometer was operated with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97, SIR97)[16] 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, and 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 in Table 1. CCDC-933035 (for **1**), -933036 (for **2**), -933037 (for **3**), and -933038 (for **4**) 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 Bruker ESP 300E X-band spectrometer equipped with an ER041XK microwave bridge, a rectangular cavity operating in T102 mode and an ER 032M field controller system. The modulation amplitude was kept well below the linewidth, and the microwave power was kept well below saturation.

Magnetic Susceptibility: Magnetic susceptibility measurements were performed with polycrystalline samples of ca. 10–20 mg by using a 6 T S700X superconducting quantum interference device (SQUID) magnetometer from Cryogenic Ltd. Magnetisation data were obtained in the temperature range 1.7–300 K under applied magnetic fields of up to 1 T. The paramagnetic contributions were obtained from the 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^{-1} for **1**–**5**, respectively.

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

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[1] *Progress in Inorganic Chemistry*, vol. 52 ("Dithiolene Chemistry: Synthesis Properties and Applications") (Ed.: E. I. Stiefel), Wiley, New York, **2004**.
[2] V. B. Mueller-Westerhoff in *Comprehensive Coordination Chemistry* (Ed.: G. Wilkinson), Pergamon Press, Oxford, **1989**, chapter 16.5, pp. 595–631.
[3] a) C. Faulmann, P. Cassoux in *Progress in Inorganic Chemistry*, vol. 52 ("Dithiolene Chemistry: Synthesis Properties and Applications") (Ed.: E. I. Stiefel), Wiley, New York, **2004**, chapter 8, pp. 399–489; b) R. Kato, *Chem. Rev.* **2004**, *104*, 5319–5346; c) P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, A. E. Underhill, *Coord. Chem. Rev.* **1991**, *110*, 115–160; d) N. Robertson, L. Cronin, *Coord. Chem. Rev.* **2002**, *227*, 93–127.
[4] S. Rabaça, M. Almeida, *Coord. Chem. Rev.* **2010**, *254*, 1493–1508.
[5] a) S. Rabaça, M. C. Duarte, I. C. Santos, L. C. J. Pereira, M. Fourmigué, R. T. Henriques, M. Almeida, *Polyhedron* **2008**, *27*, 1999–2006; b) S. Rabaça, M. C. Duarte, I. C. Santos, M. Fourmigué, M. Almeida, *Inorg. Chim. Acta* **2007**, *360*, 3797–3801; c) S. Rabaça, A. C. Cerdeira, A. I. S. Neves, S. I. G. Dias, C. Mézière, I. C. Santos, L. C. J. Pereira, M. Fourmigué, R. T. Henriques, M. Almeida, *Polyhedron* **2009**, *28*, 1069–1078; d) S. Rabaça, D. Belo, A. C. Cerdeira, S. I. G. Dias, M. B. C. Branco, L. C. J. Pereira, I. C. Santos, M. Fourmigué, M. Almeida, *CrystEngComm* **2009**, *11*, 2154–2159; e) S. Rabaça, A. C. Cerdeira, S. Oliveira, I. C. Santos, L. C. J. Pereira, J. T. Coutinho, R. T. Henriques, M. Almeida, *Polyhedron* **2012**, *39*, 91–98.
[6] a) H. Oshio, *Inorg. Chem.* **1993**, *32*, 4123–4130; b) B. Nowicka, G. Schmauch, T. Chihara, F. W. Heinemann, M. Hagiwara, Y. Wakatsuki, H. Kirsch, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2169–2175; c) O. Jeannin, R. Clérac, T. Cauchy, M. Fourmigué, *Inorg. Chem.* **2008**, *47*, 10565–10661.
[7] O. Jeannin, J. Delaunay, F. Barrière, M. Fourmigué, *Inorg. Chem.* **2005**, *44*, 9763.
[8] L. N. Dawe, J. Miglioi, L. Turnbow, M. L. Taliaferro, W. W. Shum, J. D. Bagnato, L. N. Zakharov, A. L. Rheingold, A. M. Arif, M. Fourmigué, J. S. Miller, *Inorg. Chem.* **2005**, *44*, 7530.
[9] A.-Y. Fu, D.-Q. Wang, D.-Z. Sun, *Acta Crystallogr., Sect. E* **2004**, *60*, m1869; A. M. Madalan, N. Avarvari, M. Fourmigué, R. Clérac, L. F. Chibotaru, S. Clima, M. Andruh, *Inorg. Chem.* **2008**, *47*, 940.
[10] A. C. Cerdeira, D. Simão, I. C. Santos, A. Machado, L. C. J. Pereira, J. C. Waerenborgh, R. T. Henriques, M. Almeida, *Inorg. Chim. Acta* **2008**, *361*, 3836–3841.
[11] H. Alves, D. Simão, I. C. Santos, V. Gama, R. T. Henriques, H. Novais, M. Almeida, *Eur. J. Inorg. Chem.* **2004**, 1318–1329.
[12] H. Oshio, H. Okamoto, T. Kikuchi, T. Ito, *Inorg. Chem.* **1997**, *36*, 3201–3203.
[13] D. Belo, M. J. Figueira, I. C. Santos, V. Gama, L. C. J. Pereira, R. T. Henriques, M. Almeida, *Polyhedron* **2005**, *24*, 2035–2042.
[14] a) J. V. Rodrigues, I. C. Santos, V. Gama, R. T. Henriques, J. C. Waerenborgh, M. T. Duarte, M. Almeida, *J. Chem. Soc., Dalton Trans.* **1994**, 2655–2660; b) V. Gama, R. T. Henriques, G. Bonfait, L. C. Pereira, J. C. Waerenborgh, I. C. Santos, M. T. Duarte, J. M. P. Cabral, M. Almeida, *Inorg. Chem.* **1992**, *31*, 2598–2604; c) K. Ray, E. Bill, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2005**, *127*, 5641–5654.
[15] B. Nowicka, G. Schmauch, T. Chihara, F. W. Heinemann, M. Hagiwara, Y. Wakatsuki, H. Kisch, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2169–2175.
[16] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.
[17] G. M. Sheldrick, *SHELX97 –- Programs for Crystal Structure Analysis*, release 97–2, University of Göttingen, Göttingen, Germany, **1998**.
[18] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

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