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The first coordination compound containing three different types of spin carriers: 2p–3d–4f (TCNQ$^{\cdot-}$, Cu^{2+} and Gd^{3+})

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A novel heterospin system, [{CuL}$_2$Gd(TCNQ)$_2$]·TCNQ·CH$_3$OH·2CH$_3$CN, is obtained by reacting the mononuclear complex, [CuL], with gadolinium(III) nitrate, followed by the substitution of the nitrato ions with anionic organic radicals.

The search for new compounds with exciting magnetic and photomagnetic properties prompted chemists to combine different spin carriers within the same molecular/supramolecular entity. One of the very first molecular magnets, synthesized by Kahn and coworkers, contains two different 3d spin carriers: Cu^{2+} (d^9) and Mn^{2+} (d^5),[1] while another one, reported in the same year by Miller *et al.*,[2] is a supramolecular system constructed from building blocks bearing a 3d electron, [FeCp*$_2$]$^{\cdot+}$, and a 2p electron, TCNE$^{\cdot-}$ (Cp*$^-$ = pentamethylcyclopentadienyl anion; TCNE = tetracyanoethylene). Several years later, a molecule-based magnet with a unique interlocked structure was obtained by associating two different 3d metal ions (Mn^{2+} and Cu^{2+}) and a radical (2p) cation.[3] Other systems are based on the following pairs of spin carriers: 3d–4d,[4] 3d–5d,[5] 3d–4f,[6] 3d–5f,[7] 3d–Rad$^\cdot$,[8] 4f–Rad$^\cdot$.[9] Each one of the above pair is illustrated by numerous compounds exhibiting various topologies of the paramagnetic centers and, consequently, interesting magnetic properties. Recently, Chaudhuri *et al.* have proposed a rational synthetic route to trinuclear complexes containing three different 3d paramagnetic ions.[10]

In this paper we report on the synthesis, crystal structure and the magnetic properties of the first coordination compound containing three different types of spin carriers: an organic radical (2p), a 3d metal ion (Cu^{2+}) and a rare earth ion, 4f (Gd^{3+}): [{CuL}$_2$Gd(TCNQ)$_2$]·TCNQ·CH$_3$OH·2CH$_3$CN **1** (L^{2-} = *N,N*'-propylenebis(3-methoxysalicylideneiminato); TCNQ$^{\cdot-}$ = anion of 7,7,8,8-tetracyano-*p*-quinodimethane). Compound **1** was obtained stepwise: (i) synthesis of the mononuclear copper(II) complex, [CuL]; (ii) reaction of the copper complex with gadolinium nitrate; (iii) substitution of the nitrato groups with paramagnetic TCNQ$^{\cdot-}$ anions.†

The structure of **1**‡ can be described as being constructed from almost linear trinuclear [Cu$_2$Gd] units on which the TCNQ$^{\cdot-}$ anionic radicals are attached, as shown in Fig. 1 (the value of the Cu–Gd–Cu angle is 175.96(3)°). The TCNQ$^{\cdot-}$ ions are further involved in both stacking and weak coordinative interactions, leading to a unique supramolecular architecture. The values of the interatomic distances in the TCNQ species are diagnostic of their electronic nature. For compound **1**, the carbon–carbon distances fall in the range expected for TCNQ$^{\cdot-}$ anions.[11]

Let us focus first on the [Cu$_2$Gd] moiety. The copper(II) ion is hosted within the inner compartment (the N$_2$O$_2$ site) of the organic ligand. Two [CuL] mononuclear complexes are coordinated through the empty outer O$_4$ cavities to the Gd(III) ion (two oxygen atoms arise from the phenoxo groups, the two others from the methoxy ones). The distances between the metallic centers, Cu–Gd, are equal at 3.48(4) Å. The Gd–O distances fall in the range 2.32(3)–2.61(8) Å.

One TCNQ$^{\cdot-}$ radical is coordinated to the Gd atom, which achieves a coordination number of nine [Gd(1)–N(11) 2.51(4) Å]. The second TCNQ$^{\cdot-}$ acts as a bridging ligand between copper(II) ions from neighboring [Cu$_2$Gd] units, resulting in infinite chains running along the crystallographic *a* axis. The copper(II) ions thereby achieve a coordination number of five and a square-pyramidal stereochemistry. The basal positions are occupied by the oxygen and nitrogen atoms from the compartmental ligand, while the apical positions are occupied by the nitrogen atoms arising from the TCNQ$^{\cdot-}$ groups [Cu(2)–N(5) 2.38(6) Å, Cu(1)–N(22′) 2.66(3) Å].

The third TCNQ$^{\cdot-}$ ion is uncoordinated. In Fig. 1, the TCNQ$^{\cdot-}$ groups are labeled as follows: **A**, TCNQ$^{\cdot-}$ acting as a bridge between two copper ions; **B**, TCNQ$^{\cdot-}$ coordinated to gadolinium; **C**, uncoordinated. A characteristic feature of the TCNQ$^{\cdot-}$ molecules is their tendency to stack in the solid-state.[12] The packing diagram of crystal **1** indeed shows interesting interactions at the supramolecular level (Fig. 2). The three TCNQ$^{\cdot-}$ anions corresponding to a [Cu$_2$Gd] triad are parallel and aligned with their longitudinal axis along the *b* direction. The small separations between the **A**–**B** and **B**–**C** anionic radicals (3.12 and 3.32 Å, respectively) indicate the occurrence of π–π interactions. Each TCNQ$^{\cdot-}$ radical **C** interacts further with another uncoordinated radical, **C**,′ the separation between them being 3.19 Å. Consequently, the overlap of the TCNQ$^{\cdot-}$ π clouds generate **ABCC′B′A′** stacks which connect pairs of [Cu$_2$Gd(TCNQ)$_2$]$_n^{n+}$ chains. The

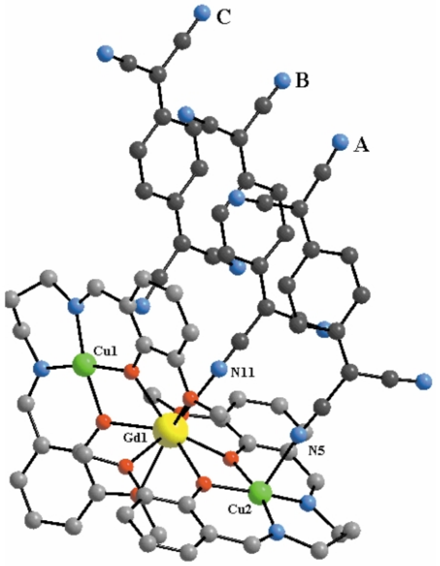

Fig. 1 View of a repeating unit in **1**. Color code: gadolinium: yellow; copper: green; nitrogen: blue; oxygen: red; carbon: grey, black.

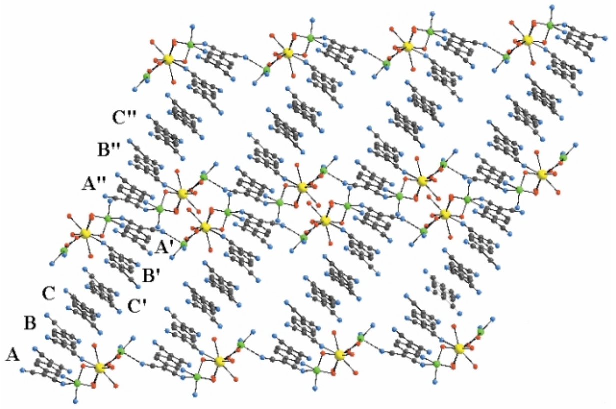

Fig. 2 Packing diagram for crystal **1** (for clarity the carbon atoms from the compartmental ligands have been removed).

propagation of the stacks through **A′–A″** interactions is somewhat weaker, due to the poor overlap of these TCNQ$^{\cdot-}$ pairs (Fig. 2) and to the longer intermolecular distance (3.45 Å).

The most intriguing properties of a heterospin system, such as complex **1**, relate to the magnetic behaviour. Magnetic susceptibility data for **1** were collected in the temperature range 2–300 K. The value of $\chi_M T$ at room temperature (9.44 cm^3 mol^{-1} K) is lower than that expected for six uncoupled spin carriers: two copper(II) ions ($S = 1/2$), one gadolinium(III) ion ($S = 7/2$) and three TCNQ$^{\cdot-}$ radicals ($S = 1/2$). The lower value of $\chi_M T$ at room temperature can be explained by strong antiferromagnetic coupling of the six stacked TCNQ$^{\cdot-}$ radicals connecting the [Cu$_2$Gd] units. This phenomenon has been observed with other compounds, where the stacking interactions between TCNQ$^{\cdot-}$ radicals lead to diamagnetic (TCNQ)$_2{}^{2-}$ dimers.[13] Considering that the TCNQ$^{\cdot-}$ ions do not contribute to the magnetic moment of **1**, the magnetic properties can be simulated by taking into account only the isolated [Cu$_2$Gd] triads.§ Indeed, the high temperature limit of $\chi_M T$ corresponds to a magnetically non-interacting Cu(II)–Gd(III)–Cu(II) (1/2–7/2–1/2) system. As the temperature is lowered, $\chi_M T$ increases, reaching a maximum of 13.0 cm^3 mol^{-1} K at 10 K (Fig. 3). This behavior indicates that the Gd(III)–Cu(II) interaction is ferromagnetic with a ground state $S = 9/2$. If only the $S = 9/2$ state is thermally populated, the expected value for $\chi_M T$ is 12.37 cm^3 mol^{-1} K, a value which is close to the experimental one at $T = 10$ K (considering, in a first approximation, $g_{Cu} = g_{Gd} = 2$). Below 10 K, $\chi_M T$ decreases, indicating the onset of intermolecular antiferromagnetic interactions and/or the splitting of the $S = 9/2$ ground state in zero field.

For a linear [Cu(II)Gd(III)Cu(II)] system, the energies of the low-lying states are obtained by using the isotropic spin Hamiltonian: $\boldsymbol{H} = -J(\mathbf{S}_{Cu1}\mathbf{S}_{Gd} + \mathbf{S}_{Gd}\mathbf{S}_{Cu2})$. Least-squares fit to the data, between 10 and 300 K, leads to $J = +7.7$ cm^{-1}, $g_{Cu} = 2.17$, $g_{Gd} = 2.03$, the reliability factor being $R = 1.3 \times 10^{-5}$. The magnetic coupling between Gd(III) and Cu(II) ions is now well documented.[14] In most cases, this interaction was found to be ferromagnetic.

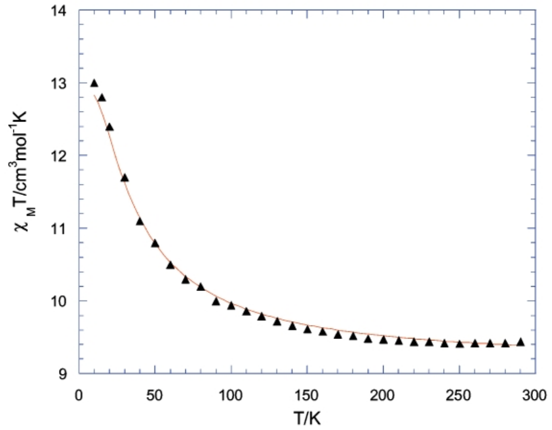

Fig. 3 Magnetic behavior of compound **1** between 10 and 300 K ($\chi_M T$ *vs.* T plot). The solid line was generated from the best-fitting magnetic parameters.

The heterospin compound described here in opens interesting perspectives to the magnetochemistry of 2p–3d–4f systems. Moreover, the results presented above show that heteronuclear complexes can be used as building-blocks in constructing coordination polymers, by linking the 3d–4f discrete entities through appropriate bridging ligands.

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Notes and references

† Preparation of [{CuL}$_2$Gd(TCNQ)$_2$]·TCNQ·CH$_3$OH·2CH$_3$CN **1**: the [CuGdL(NO$_3$)$_3$] precursor was obtained following the general procedure reported by Costes *et al.*[14b] and LiTCNQ was obtained according to ref. 15 A solution of LiTCNQ (0.15 g, 0.7 mmol) in 15 mL of methanol–acetonitrile (1 : 1), was added dropwise to a solution of [CuGdL(NO$_3$)$_3$] (0.3 g, 0.4 mmol) dissolved in 45 mL of methanol–acetonitrile. The reaction was carried out under oxygen-free nitrogen, using standard Schlenk techniques and degassed solvents. The resulting mixture was allowed to stand in the refrigerator. After 5 days, dark-blue crystals resulted, which were filtered off and washed with methanol–acetonitrile (1 : 1).

‡ *Crystal data* for **1**: C$_{79}$H$_{62}$Cu$_2$GdN$_{18}$O$_9$, triclinic, space group $P\bar{1}$, $a = 12.884(3)$, $b = 17.663(4)$, $c = 18.225(4)$ Å, $\alpha = 111.46(3)$, $\beta = 99.24(3)$, $\gamma = 104.03(3)°$, $V = 3599.26(12)$ Å^3, $Z = 2$; $D_c = 1.560$ g cm^{-3} $F(000) = 1710$; $\mu = 1.57$ mm^{-1}; $R_1 = 0.0695$ for 12976 data [$I > 4\sigma(I)$], and 0.0809 for all 14557 data. The diffraction intensities were collected at 200(2) K on a Huber four-circle cradle equipped with a BRUKER SMART CCD detector. The structure was solved using the program SHELXS-97 and refined using the program SHELXL-97. CCDC reference number 179905. See http://www.rsc.org/suppdata/cc/b2/b202628g/ for crystallographic data in CIF or other electronic format.

§ The alternative charge distribution, Cu^I ($S = 0$)–Gd^{III} ($S = 7/2$)–Cu^I ($S = 0$)–TCNQ$^{\cdot-}$ ($S = ½$)–2TCNQ^0 ($S = 0$), is not supported by the magnetic data: both high- and low-temperature limits of $\chi_M T$ do not correspond to this electronic structure.

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