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Single ion magnet behaviour in a two-dimensional network of dicyanamide-bridged cobalt(II) ions†

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A novel two-dimensional coordination polymer of the formula $[Co(dca)_2(atz)_2]_n$ (1) resulted from assembling *trans*-bis(2-amino-1,3,5-triazine)cobalt(II) motifs by dicyanamide spacers. Variable-temperature dc and ac magnetic susceptibility measurements of 1 show that the high-spin cobalt(II) ions act as single ion magnets (SIMs).

In recent years, dicyanamide (dca)-bridged coordination compounds have attracted significant attention for their intriguing architectures and topologies as well as for a large variety of magnetic properties.[1,2] The binary metal-dicyanamide complexes with a 3D-rutile type architecture (α-$[M(dca)_2]$), formed by six-coordinate metal ions and three-connecting spacers ($\mu_{1,3,5}$-dca ligands) in the 1 : 2 metal to dca molar ratio, exhibit a broad diversity long-range magnetic ordering at very low temperatures.[3] This magnetic behaviour depends on the nature of the metal ion, being weakly ferromagnetic [Co(II), Cu(II) and Ni(II)][4] or spin-canted antiferromagnetic [Cr(III), Mn(II) and Fe(II)].[5] The modification of the M-dca networks by the incorporation of N-donors as bridges or terminal co-ligands into the structures resulted in the formation of numerous architectures of the general formula $[M(dca)_2(L)_n]$ (n = 1 or 2), including linear chains with a single or a double $\mu_{1,5}$-dca connectors, 2D (4,4) nets and herringbone-like lattices with a single $\mu_{1,5}$-dca bridge, triangular lattices with $\mu_{1,3,5}$- and $\mu_{1,5}$-dca linkers, and also 3D networks.[6–8] In contrast to the binary α-$[M(dca)_2]$ systems, the large number of magneto-structurally investigated heteroleptic compounds display very weak antiferromagnetic couplings (J less than 1 cm^{-1}) because of the poor ability of the extended $\mu_{1,5}$-dca bridges to mediate electronic interactions.[1a,2e,5c,7a]

Having in mind the recent research results dealing with a few magneto-structural studies of mono- and polynuclear Co(II) compounds where the metal ions exhibit slow relaxation of the magnetization behaving as single ion magnets (SIMs),[9–12] we have used the dca anion and the 2-amino-1,3,5-triazine (atz) molecule as a linker and an end-cap ligand, respectively. The resulting two-dimensional coordination polymer of the formula $[Co(dca)_2(atz)_2]_n$ (**1**) has been characterized by spectroscopic techniques, X-ray diffraction and magnetic measurements.

Compound **1** was prepared‡ by the reaction of an aqueous solution of Na(dca) with a methanolic solution of $CoCl_2{\cdot}2H_2O$ and 2-amino-1,3,5-triazine (atz) in a 2 : 1 : 2 dca : Co(II) : atz molar ratio.‡ Intense absorptions associated with the ν_{as} + ν_s(C≡N), ν_{as}(C≡N) and ν_s(C≡N), stretching modes of dca ligands occur at 2312, 2263 and 2194 cm^{-1}, respectively. Their shift towards higher frequencies as compared to those of the sodium dicyanamide (2286, 2232 and 2179 cm^{-1}) supports the coordination of dca in **1**. The XRPD pattern measured for the as-synthesized sample was in good agreement with the XRPD patterns simulated from the respective single-crystal X-ray data using the Mercury 2.4 program,[13] demonstrating that the crystal structure is truly representative of the bulk material (ESI, Fig. S1†).

The single crystal X-ray analysis (see Table S1, ESI†) revealed a polymeric structure consisting of neutral layers of the formula $[Co(dca)_2(atz)_2]$ which are interlinked into a supramolecular 3D structure by hydrogen bonding between the coordinated atz ligands and the central nitrogen atoms of the dca bridges [N(4)–H(4B)···N(97)^e with values for D···A and D–H···A of 3.083(3) Å and 164.0°, respectively; symmetry code: (e) = −1/2 + x, 1/2 + y, −1/2 + z] (Fig. S2a†) and π–π stacking interactions with centroid–centroid distances of 3.573 and 3.744 Å (Fig. S2b, ESI†).

Each cobalt(II) ion, located at the crystallographic inversion Wyckoff 4d center, is six-coordinate with four nitrile nitrogen

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†Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format, materials and methods, figures of XRPD, IR, UV-Vis and structure and crystallographic data (refinement conditions and bond lengths and angles) and a table of selected magneto-structural data of dca-bridged cobalt(II) complexes. CCDC 993408. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt03574g

atoms at equatorial sites [Co–N distances of 2.0887(17) and 2.0968(16) Å] and two nitrogen atoms of the atz ligand at the axial sites [Co–N distance of 2.1677(15) Å] (see Table S2, ESI†), building an elongated octahedron (Fig. 1a). The dca ligands adopt the $\mu_{1,5}$ bridging mode and they connect each metal ion to other four neighbouring metal centers leading to distorted rhombus-grid sheets parallel to the crystallographic *bc* plane (Fig. 1b). The metal centers create 4-c uninodal net described by a $\{4^2;6^2\}$ Schläfli symbol and a [4.4.4.4.6(2).6(2)] extended point vertex symbol, which corresponds to the **sql** topological type.[14]

Within the $[Co(II)]_4$ units, the equatorial coordination planes of the neighboring metal centers are almost perpendicular, exhibiting a dihedral angle of 88.88°. The intralayer Co···Co separation through the dca bridge is 8.041 Å, whereas the metal–metal distances through the diagonals are different (13.423 and 8.859 Å), indicating that metal centers in the $[Co(II)]_4$ units adopt a rhombus arrangement rather than a square disposition. Intralayer hydrogen bonds [N(4)–H(4A)···N(2)^f with D···A = 3.209(3) Å and D–H···A = 174.0°; symmetry code: (f) = 1/2 − *x*, 1/2 − *y*, 1 − *z*] contribute to the stabilization of the neutral layers. The shortest interlayer Co···Co^g [symmetry code: (g) = 1/2 + *x*, 1/2 + *y*, *z*] separation is 8.602 Å.

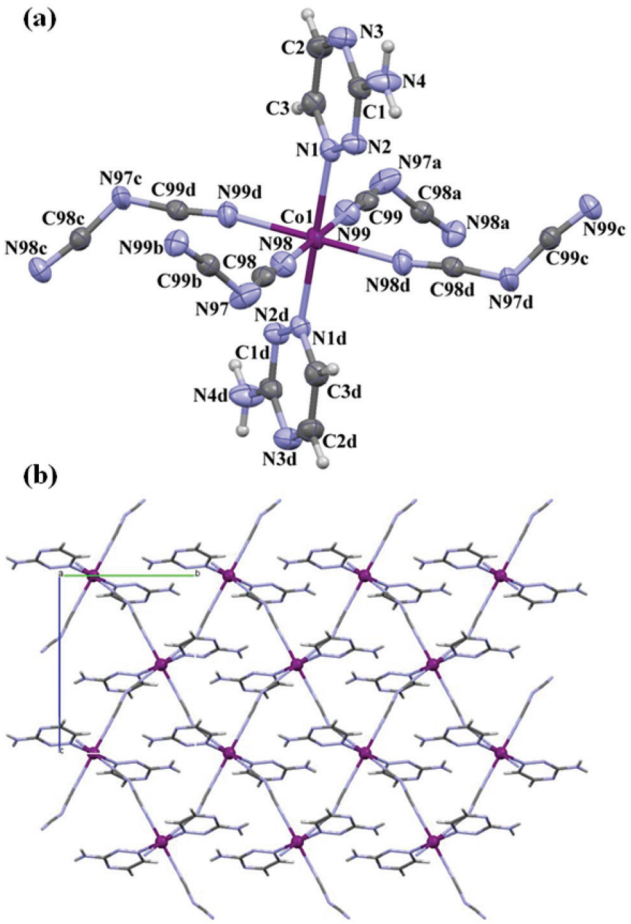

Fig. 1 (a) Perspective view of the metal environment in **1** together with the atom numbering. Displacement ellipsoids are drawn at 50% probability level [symmetry code: (a) = *x*, –*y*, –1/2 + *z*; (b) = *x*, –*y*, 1/2 + *z*; (c) = 1/2 − *x*, –1/2 + *y*, 1/2 − *z*; (d) = 1/2 − *x*, –1/2 − *y*, 1 − *z*]. (b) View of a fragment of the 2D structure of **1** formed by $\mu_{1,5}$-dca bridges.

The magnetic properties of **1** in the form of a $\chi_M T$ *versus* *T* plot [χ_M is the magnetic susceptibility per Co(II) ion] are shown in Fig. 2. At room temperature $\chi_M T$ is equal to 2.77 cm^3 mol^{-1} K [μ_{eff} = 4.71 BM to be compared with μ_{eff} (spin only g = 2.0) = 3.87 BM]. This value is within the range of those observed for six-coordinate high-spin cobalt(II) complexes with an unquenched angular momentum.[15] Upon cooling, $\chi_M T$ remains practically constant in the high temperature range and it decreases sharply below 150 K to reach a value of 1.78 cm^3 mol^{-1} K at 1.9 K. No maximum of the magnetic susceptibility is observed in the χ_M *vs.* *T* plot. The decrease of $\chi_M T$ in **1** can be due to an antiferromagnetic interaction between the cobalt(II) ions and/or to the thermal depopulation of the higher energy Kramers doublets of the cobalt(II) centers.

Having in mind the previous magneto-structural results concerning the dca-bridged cobalt(II) compounds (see Table S3, ESI†) and the large intra [*ca.* 8.0 Å across the single $\mu_{1,5}$-dca bridge] and interlayer [shortest value about 8.6 Å] cobalt–cobalt separation, the magnetic interaction between the local spin quartets, if any, is expected to be very weak. Consequently, the magnetic data of **1** were analysed through the Hamiltonian of eqn (1):[16]

$$\boldsymbol{H} = -\alpha\lambda \boldsymbol{L}_{Co}\boldsymbol{S}_{Co} + \Delta[\boldsymbol{L}^2{}_{z,Co} - 1/3L(L+1)] + \beta H(-\alpha \boldsymbol{L}_{Co} + g_e \boldsymbol{S}_{Co}) \quad (1)$$

where λ is the spin–orbit coupling and α is an orbital reduction factor defined as $\alpha = A\kappa$. The κ parameter considers the reduction of the orbital momentum caused by the delocalization of the unpaired electrons and the *A* parameter contains the admixture of the upper $^4T_{1g}(^4P)$ state into the $^4T_{1g}(^4F)$ ground state (*A* = 1.5 and 1 in the weak and strong crystal-field limits, respectively). Δ is the energy gap between the singlet $^4A_2$ and doublet ^4E levels arising from the splitting of the triplet orbital $^4T_{1g}$ ground state under an axial distortion of the

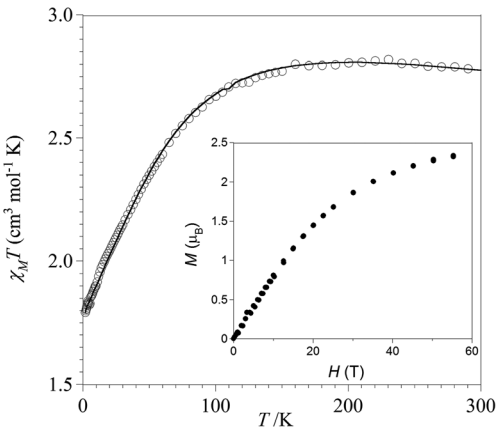

Fig. 2 Temperature dependence of the $\chi_M T$ product for **1**: (o) experimental; (—) best-fit curve through eqn (1) (see text). The inset shows the magnetization *vs.* *H* plot 2.0 K.

ideal O_h symmetry of the cobalt(II) ion. The best-fit parameters using the experimental data in the whole temperature range investigated are: α = 1.18(1), λ = −125(1) cm^{-1} and Δ = −509(10) cm^{-1}. Given that the values of Dq (955 cm^{-1}) and B (890 cm^{-1}) could be obtained through the analysis of the UV-Vis-NIR electronic spectrum of **1** (see Fig. S4, ESI†), a value of A = 1.41 can be calculated through eqn (2) and (3):[16]

$$c = 0.75 + 1.875B/Dq - 1.25[1 + 1.8B/Dq + 2.25(B/Dq)^2]^{1/2} \quad (2)$$

$$A = (3/2 - c^2)/(1 + c^2) \quad (3)$$

and then κ is found to be equal to 0.84.

The value of the magnetisation *vs.* H plot for **1** at 2.0 K tends to a quasi-saturation value of 2.08 BM at 6 T (inset of Fig. 2), a value which is as expected, S_{eff} = 1/2 with g_{av} *ca.* 4.2. In this respect, it deserves to be noted that the maximum value of the saturation magnetisation in the M against H plots ($M_{sat} = g_0\beta M_S$) as a function of the temperature T < 30 K [a situation where the ground doublet for a six-coordinate high-spin cobalt(II) ion is the only populated state] would be 2.06 BM with $g_0 = (10 + 2\alpha)/3 = 4.12$.

The ac susceptibility measurements for **1** under a 0 G static field show no out-of-phase (χ_M'') signals suggesting a fast tunnelling of the magnetization (QTM). The application of a dc field of 1000 G removes the QTM and the frequency dependence of χ_M'' is observed (Fig. 3a). The relaxation times obtained from the maxima of χ_M'' were fitted to an Arrhenius law (Fig. 3b), giving values for the energy barrier (E_a) and pre-exponential factor (τ_0) of 5.1 cm^{-1} and 1.7 × 10^{-6} s, respectively.

In conclusion, the X-ray structure of a novel 2D coordination polymer of the formula $[Co(atz)_2(dca)_2]_n$ (**1**) with the cobalt(II) ions bridged by $\mu_{1,5}$-dca bridges has been reported. Combined dc and ac variable-temperature magnetic susceptibility measurements reveal the SIM behaviour of the magnetically isolated six-coordinate high-spin cobalt(II) ions. Further work will be undertaken to increase the reduced number of magnetic coordination polymers of Co(II) behaving as SIMs by using the synthetic route described herein aiming to gain deeper insights into these interesting magnetic systems.

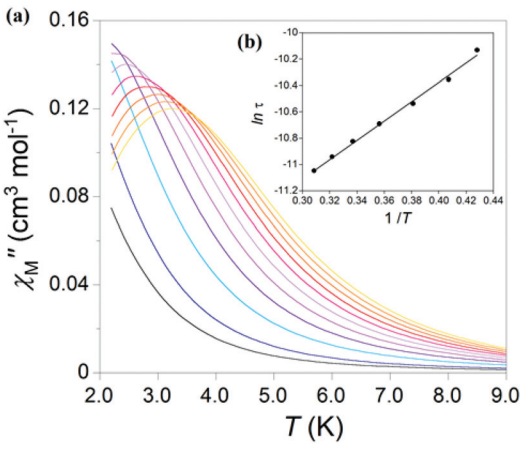

Fig. 3 (a) Frequency dependence of the out-of-phase ac susceptibilities from 2.0 to 9.0 K under a 1000 Oe dc field for **1**. (b) The relaxation time of the magnetization ln(τ) against 1/T for **1**. The solid line represents the Arrhenius plot.

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Notes and references

‡Synthesis: An aqueous solution (5 mL) of $NaN(CN)_2$ (0.180 g, 2 mmol) was slowly poured into a methanolic solution (15 mL) containing $CoCl_2{\cdot}2H_2O$ (0.240 g, 1 mmol) and 3-amino-1,2,4-triazine (0.192 g, 2 mmol) under continuous stirring for several hours. The resulting pink solution was filtered to remove any small solid particle and allowed to evaporate in a hood at room temperature. X-ray quality pink prisms of **1** were grown from the mother liquor and collected after two weeks. Yield: 70% on Co. Elemental analysis (%) for $C_{10}H_8N_{14}Co$ (**1**): Calcd: C, 31.34; H, 2.10; N, 51.17; Found: C, 31.52; H. 2.19; N, 51.99. IR (KBr, cm^{-1}): 3400(s), 3319(s) and 3215(s) [ν(NH)]; 2311(s) [ν_{as} + ν_s(C≡N)]; 2262(s) [ν_{as}(C≡N)] and 2194(vs) [ν_s(C≡N)], 1631(s), 1586 (w), 1560 (m), 1542(w) and 1527 (w) [ν(C=N)] and [ν(C=C)]. UV-Vis-NIR (solid, nm): 1020, 427, 355, 302 and 217.

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