A novel two-dimensional coordination polymer of the formula [Co(dca)₂(atz)₂] (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. The binary metal-dicyanamide complexes with a 3D-rutile type architecture [α-[M(dca)₃]] were formed by six-coordinate metal ions and three-connecting spacers (µ₁,₃,₅-dca ligands) in the 1:2 metal to dca molar ratio, exhibit a broad diversity long-range magnetic ordering at very low temperatures. This magnetic behaviour depends on the nature of the metal ion, being weakly ferromagnetic [Co(II), Cu(II) and Ni(II)] or spin-canted antiferromagnetic [Cr(III), Mn(II) and Fe(II)]. The modification of the M-dca networks by the incorporation of N-donors as bridges or terminal coligands 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 µ₁,₅-dca connectors, 2D (4,4) nets and herringbone-like lattices with a single µ₁,₅-dca bridge, triangular lattices with µ₁,₃,₅ and µ₁,₅-dca linkers, and also 3D networks. In contrast to the binary α-[M(dca)₃] systems, the large number of magneto-structurally investigated heteroleptic compounds display very weak antiferromagnetic couplings \( J < 1 \text{ cm}^{-1} \) because of the poor ability of the extended µ₁,₅-dca bridges to mediate electronic interactions.

Having in mind the recent research results dealing with a few magneto-structural studies of mono- and polymeric metal ions compounds where the metal ions exhibit slow relaxation of the magnetization behaving as single ion magnets (SIMs), 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] (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 CoCl₂·2H₂O and 2-amino-1,3,5-triazine (atz) in a 2:1:2 dca:Co(II):atz molar ratio.‡ Intense absorptions associated with the \( ν\text{at} + ν\text{N}(C=\text{N}) \) and \( ν\text{at} + \nu\text{at}(C=\text{N}) \), stretching modes of dca ligands occur at 2312, 2263 and 2194 \( \text{cm}^{-1} \), respectively. Their shift towards higher frequencies as compared to those of the sodium dicyanamide (2286, 2232 and 2179 \( \text{cm}^{-1} \)) 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, 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 \([N(4)−H(4B)⋯N(97)]^\text{e}^\text{e} \) with values for D⋯A and D−H⋯A of 3.083(3) Å and 164.0°, respectively; symmetry code: \( (e) = -1/2 + x, 1/2 + y, -1/2 + z \). In 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
atoms at equatorial sites [Co–N distances of 2.0887(17) and 2.0968(16) Å] and two nitrogen atoms of the az 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 μ1,3 bridging mode and they connect each metal ion to other four neighbouring metal centers leading to distorted rhombohedral 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 [4.4.4.6(2),6(2)] extended point vertex symbol, which corresponds to the sq1 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)] 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 separation [symmetry code: (g) = 1/2 + x, 1/2 + y, z] separation is 8.602 Å.

The magnetic properties of 1 in the form of a χM T versus T plot (χM is the magnetic susceptibility per Co(II) ion) are shown in Fig. 2. At room temperature χM T is equal to 2.77 cm³ mol⁻¹ K [μeff = 4.71 BM to be compared with μeff (spin only γ = 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, χM T remains practically constant in the high temperature range and it decreases sharply below 150 K to reach a value of 1.78 cm³ mol⁻¹ K at 1.9 K. No maximum of the magnetic susceptibility is observed in the χM vs. T plot. The decrease of χM 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 μ1,5-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

$$H = -\alpha L_{6e}S_{Co} + \Delta [L^2_{z,Co} - 1/3L(L + 1)] + \beta H(-\alpha L_{6e} + g_{eff}S_{Co})$$

(1)

where λ is the spin–orbit coupling and α is an orbital reduction factor defined as α = Aκ. The κ parameter considers the reduction of the orbital momentum caused by the delocalization of the unpaired electrons and the parameter contains the admixture of the upper ⁴T₁g(⁴P) state into the ⁴T₁g(⁴F) ground state (κ = 1.5 and 1 in the weak and strong crystal-field limits, respectively). Δ is the energy gap between the singlet ⁴A₂ and doublet ⁴E levels arising from the splitting of the triplet orbital ⁴T₁g ground state under an axial distortion of the
ideal $O_h$ symmetry of the cobalt(n) ion. The best-fit parameters using the experimental data in the whole temperature range investigated are: $\alpha = 1.18(1)$, $\lambda = -125(1)$ cm$^{-1}$ and $\Delta = -509(10)$ 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):

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

(2)

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

(3)

and then $\kappa$ 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 ($M_{sat} = g_0BM_0$) as a function of the temperature $T < 30 \, K$ [a situation where the ground doublet for a six-coordinate high-spin cobalt(n) 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 ($\chi''_M$) 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 $\chi''_M$ is observed (Fig. 3a). The relaxation times obtained from the maxima of $\chi''_M$ were fitted to an Arrhenius equation polymer of the formula $\text{[Co(atz)$_2$(dca)$_2$]}_n$ (1) with the cobalt(n) ions bridged by $\mu_1\mu_2$-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(n) ions. Further work will be undertaken to increase the reduced number of magnetic coordination polymers of Co(n) behaving as SIMs by using the synthetic route described herein aiming to gain deeper insights into these interesting magnetic systems.

Acknowledgements

This work was supported by the Polish National Science Centre (grant no. 2012/07/N/ST5/02213), the Ministerio Español de Ciencia e Innovacion (Project CTQ2013-44844P) and the Generalitat Valenciana (PROMETEOII/2014/070). Joanna Palion-Gazda is grateful for the scholarship from the DoktorIS project co-financed by the European Social Fund.

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$_2$·2H$_2$O (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 solid oxide 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$_8$N$_{14}$Co: C, 42.2; H, 2.0; N, 51.7;

$\Delta_f^1$ [c(NHa)Co]: 1631(s), 1586 (w), 1560 (m), 1542(w) and 875 cm$^{-1}$; $\Delta_f^2$ [c(NH)]: 1631(s), 1586 (w), 1560 (m), 1542(w) and 875 cm$^{-1}$; $\Delta_f^J$ [C(C=N)], 1631(s), 1586 (w), 1560 (m), 1542(w) and 1527 (w). UV-Vis-NIR (solid, nm): 1020, 427, 355, 302 and 217.


