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A novel mixed-valence complex containing $Co^{II}_2Co^{III}_2$ molecular squares with 4,5-imidazoledicarboxylate bridges†

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A heterometallic complex, $Na_2[Co^{II}_2Co^{III}_2(IDC^{3-})_4(bipy)_4]\cdot 12H_2O$ (bipy = 2,2′-bipyridine), in which mixed-valence tetranuclear squares with imidazoledicarboxylate (IDC^{3-}) linkers are tethered into a unique chain through disodium units, is hydrothermally synthesized and structurally and magnetically characterized.

In the last decade, with the rapid development of supramolecular and coordination chemistry, syntheses of high-symmetry metallacycles, such as triangles, squares, boxes and polyhedra, have attracted much attention. By combining two different precursor building blocks named angular unit (A) and linear unit (L), respectively, the former with a right angle and the latter with two symmetrical active sites, various molecular squares have been achieved.[1] The majority of them are based on the Pt(II) or Pd(II) metal ions in the square planar configuration and linear ditopic linkers with two monodentate donating sites. Many efforts have also been made to explore the assembly of molecular squares from octahedral transition metals, and according to the coordination mode, most of the linkers applied so far fall into two main types: i) rigid bis(tridentate) linkers that fast clip the metal ions at the corners and thus may result in squares with perfect co-planarity;[2] ii) linkers in which at least one of the coordinative sites is monodentate, the co-planarity of the resultant square being less perfect.[3] However, the assembly of molecular squares from bis(bidentate) linkers is rare and remains a challenge.[4] In principle, bis(bidentate) linkers with appropriately oriented chelating sites can also lead to molecular squares, with the octahedral coordination metals being terminated by bidentate ligands. This rationale has been used to assemble a chiral square from a rotationally flexible linker that has two bidentate sites pointing in opposite directions.[4] The potential of assembling molecular squares with perfect co-planarity from rigid bis(bidentate) linkers leads us to this interesting and challenging frontier.

We are interested in the solid-state coordination chemistry of imidazoledicarboxylic acid (H_3IDC), which remains largely unexplored[5] although it is rather simple and has great potential for coordinative interaction and hydrogen bonding. It can be successively deprotonated to generate H_2IDC^-, $HIDC^{2-}$ and IDC^{3-}, dependent on the pH level, and hence may result in a large diversity of molecular or supramolecular architectures. In particular, the fully deprotonated ion, IDC^{3-}, which is planar and has a two-fold axis bisecting the imidazole ring, contains two bidentate sites that point in different directions co-planar to each other. Geometrically, such a ligand should be a good linker for constructing rigid molecular squares. Herein we report a heterometallic complex containing molecular squares with IDC^{3-} as linkers.

The complex, $Na_2[Co^{II}_2Co^{III}_2(IDC^{3-})_4(2,2'\text{-bipy})_4]\cdot 12H_2O$ (**1**), was synthesized *via* a hydrothermal method.‡ X-Ray analysis§ revealed that the complex contains a unique mixed-valence molecular square in which Co(II) and Co(III) alternate at the corners. As shown in Fig. 1, there are two crystallographically independent cobalt ions, each being octahedrally coordinated by two nitrogen atoms from a terminal bipy, two nitrogen and two oxygen atoms from two individual IDC^{3-} ligands. The Co–O and Co–N bond lengths around Co2 (1.88–1.94 Å) are remarkably shorter than those around Co1 (2.09–2.13 Å), suggesting that Co1 and Co2 are Co^{II} and Co^{III}, respectively. This is further supported by the axially elongated distortion of the geometry around Co1, due to the Jahn–Teller effect of the Co^{II} (d^7) ion. Each IDC^{3-} anion is quasi-planar and connects a Co(II) and a Co(III) ion in a bis(bidentate) mode, with the Co–N–C–C–O chelating rings being essentially coplanar with the imidazole ring, the dihedral angles not exceeding 2.9°. Thus, two Co(II) and two Co(III) ions, with bipy as terminal ligands, play the roles of angular units, and four IDC^{3-} ions behave as rigid linear units, generating such a molecular square (Fig. 2) that resides

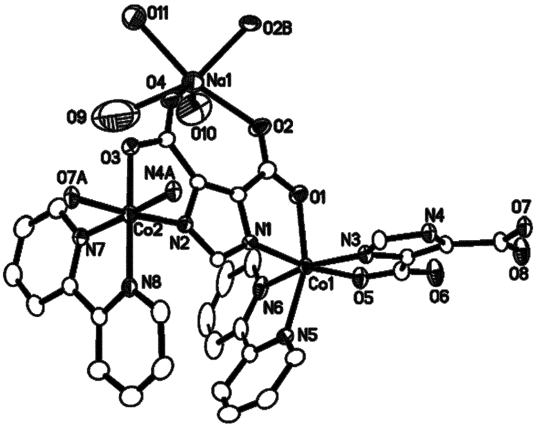

Fig. 1 Coordination environment of the cobalt and IDC^{3-} ions. Selected bond distances (Å) and angles (°): Co1–N3 2.089(4); Co1–O5 2.099(3); Co1–N1 2.110(4); Co1–N6 2.109(4); Co1–N5 2.127(4); Co1–O1 2.133(3); Co2–N2 1.878(4); Co2–N4A 1.890(4); Co2–O7A 1.908(3); Co2–O3 1.911(3); Co2–N8 1.931(4); Co2–N7 1.939(4). O1–Co1–N5 158.73(15); O3–Co2–N8 173.76(16). Hydrogen atoms are omitted for clarity. Symmetry codes: A, $1 - x, 1 - y, 1 - z$; B, $1 - x, y, 1.5 - z$.

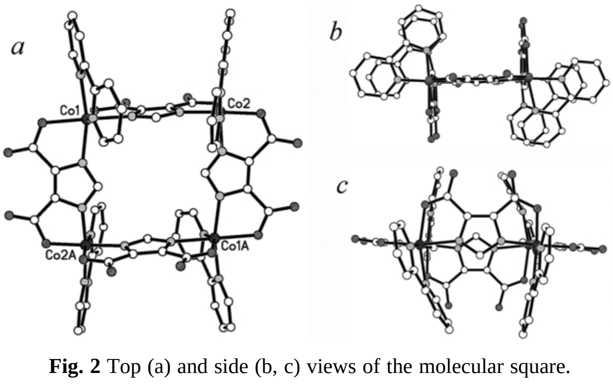

Fig. 2 Top (a) and side (b, c) views of the molecular square.

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† Electronic supplementary information (ESI) available: TGA diagram and χT *vs.* T plot of the compound. See http://www.rsc.org/suppdata/cc/b3/b315357f/

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on an inversion center and hence the four metal ions are exactly coplanar. The lateral Co(II)···Co(III) lengths of the Co_4 square are 6.18 and 6.17 Å, the diagonal Co(II)···Co(II) and Co(III)···Co(III) distances are 8.40 and 9.06 Å, respectively, and the vertex angles are 94.3° for Co(III)–Co(II)–Co(III) and 85.7° for Co(II)–Co(III)–Co(II), indicating only slight deviations from the ideal square geometry. Interestingly, the flattened linkers assume two different orientations relative to the square plane. Two opposite and antiparallel linkers are nearly in the square plane, with the dihedral angle being only 6.1°. The C–H groups of the two linkers point towards the square center, with the H atoms separated by 3.32 Å. To meet the geometric requirements of the octahedral coordination, the other two opposite and antiparallel linkers are disposed perpendicular to the square plane in an up-and-down fashion (Fig. 2c). Such a configuration of molecular squares, owing to the rigidity of the IDC^{3-} linker and the specific orientations of the coordination sites, is unprecedented. Lying between the neighboring squares related by a 2-fold axis parallel to the *b* axis, are two carboxylate μ_2-O bridged Na^+ ions that are situated at the same 2-fold axis. Each sodium ion is six-coordinated by three water molecules and three carboxylate oxygens from two adjacent squares with a severely distorted octahedral environment. The disodium units serve as “hinges” that tether the molecular squares into a chain along the *c* axis (Fig. 3). The dihedral angle and the center-to-center distance between neighboring squares are 26.5° and 9.39 Å, respectively. Between the chains, there exist ordered and disordered water molecules that hydrogen-bond to the carboxylate groups or the coordinated water molecules.

The thermal gravimetric analysis (TGA) revealed two distinct mass loss regions centered around 55 and 100 °C, respectively. The total mass loss before 160 °C (*ca.* 11.7%) is in agreement with the water content (12.45%) calculated according to the X-ray analysis. The infrared absorptions of the carboxylate groups appear at *ca.* 1652 and 1459 cm^{-1} for the ν_{as} and ν_s modes, respectively. The magnetic properties were measured over 2–300 K.† The χT product per square (6.13 emu mol^{-1} K, χ is the magnetic susceptibility) at room temperature is significantly larger than the spin-only value for two $S = 3/2$ ions (3.76 emu mol^{-1} K), but slightly smaller than the value expected for two free Co(II) ions with negligible spin–orbit coupling (6.76 emu mol^{-1} K), indicating significant contributions from the orbital momentum, typical of the Co(II) ion ($^4T_{1g}$) in an octahedral field. This also confirms that the square contains two paramagnetic Co(II) ions and two diamagnetic Co(III) ions. Upon cooling, the χT value decreases monotonously and reaches 5.81 emu mol^{-1} K at 2 K. Since the Co(II) ions are placed at the diagonal vertexes and thus well separated, the magnetic interaction between Co(II) ions should be negligible, if any. The temperature-dependent behavior should be mainly due to the combination of the spin–orbit coupling and the low-symmetry ligand field effects that cause splitting of the $^4T_{1g}$ levels.[6] Another interesting feature of the square is the presence of the mixed valences. To our knowledge, the present complex is the first example that contains mixed-valence $Co^{II}Co^{III}$ molecular squares. However, the insolubility of the complex in water and organic solvents prevents us from measuring its electrochemical properties.

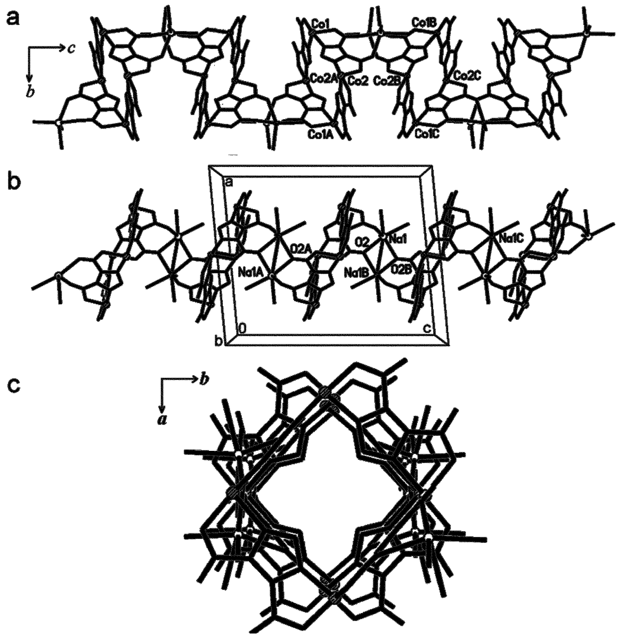

Fig. 3 Views of the chain along the *a*, *b* and *c* directions. The terminal 2,2′-bipy ligand and H atoms are omitted for clarity. Symmetry code: A, $1 - x$, $1 - y$, $1 - z$; B, $1 - x$, y, $1.5 - z$; C, x, $1 - y$, $0.5 + z$.

In summary, we have presented a novel heterometallic and mixed-valence complex with “chain of squares” topology, in which tetranuclear $Co^{II}_2Co^{III}_2$ squares with imidazoledicarboxylate linkers are tethered into chains by disodium units. We are currently extending this work to more transition metals.

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Notes and references

‡ Preparation and analytical data for **1**: To a mixture of H_3IDC (0.5 mmol, purchased from Acros), NaOH (1.0–2.0 mmol) or NaOH–Et_3N (1.0 and 0.25 mmol, respectively), and deionized water (10 mL) in a 23 mL Teflon-lined bomb, were added $Co(OAc)_2 \cdot 4H_2O$ (0.062 g, 0.25 mmol) and 2,2′-bipy (0.039 g, 0.25 mmol). The bomb was sealed and kept at 150 °C for 7 days. The final pH value of the reaction mixture ranges from 7 to 9. Red crystals of hexagonal tablet shape were collected and washed by deionized water. The typical yield is 78%. Anal. Calcd for **1**: C, 41.54; H, 3.49; N, 12.92%. Found: C, 41.18; H, 3.60; N, 12.75%.

§ Crystal data for **1**: $Na_2[Co^{II}_2Co^{III}_2(IDC^{3-})_4(bipy)_4]\cdot 12H_2O$, M_r = 1734.94, monoclinic, space group $C2/c$, a = 15.1152(3) Å, b = 25.5074(5) Å, c = 18.7706(4) Å, β = 95.3476(10)°, U = 7205.5(3) Å^3, T = 293 K, Z = 4, ρ_{calcd} = 1.599 Mg m^{-3}, μ(Mo–Kα) = 1.012 mm^{-1}, S = 0.964, 68626 reflections measured, 7621 unique (R_{int} = 0.1111), R_1 = 0.0582, wR_2 = 0.1940 (all data). CCDC 225921. See http://www.rsc.org/suppdata/cc/b3/b315357f/ for crystallographic data in .cif format.

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