Triazolopyridines as ligands: structural diversity in iron(II), cobalt(II), nickel(II) and copper(II) complexes of 3-(2-pyridyl)-[1,2,4]triazolo[4,3-\textit{a}]pyridine (L\textsuperscript{10}) and spin crossover in \([\text{Fe}^{\text{II}}(L^{10})_2(\text{NCS})_2]\]

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**Fig. S1.** Views of the three different coordination environments (N_{12}, N_9 and N_8) found in [Eu^{II}(II)_2] (1). Hydrogen atoms have been omitted for clarity.

**Fig. S2.** View of the molecular structure of [Fe^{III}(IV)_2(NCS)_{2}(MeOH)_{2}] (2). Hydrogen atoms have been omitted for clarity.

**Fig. S3.** View of the molecular structure of [Cu^{II}(L)_{2}Cl] (3). Hydrogen atoms have been omitted for clarity.
**Fig. S4.** View of the molecular structure of $[\text{Ag}^{+}_2(L^4)_2(\text{NO}_3)_2]$ (4). Hydrogen atoms have been omitted for clarity.

**Fig. S5.** View of the molecular structure of $[\{\text{Cu}^{II}(L^5)_2(\text{HCO}_2)\}_2(\mu-\text{HCO}_2)_2]\cdot 4\text{H}_2\text{O}$ (5). Hydrogen atoms, except those of the $\text{HCO}_2^-$ co-ligands, and solvate molecules have been omitted for clarity.

**Fig. S6.** View of the molecular structure of $[\text{Cu}^{I}_4(L^6)_4(\mu-\text{Br})_2(\mu_3-\text{Br})_2]$ (6). Hydrogen atoms have been omitted for clarity.
**Fig. S7.** View of the molecular structure of $[\text{Cu}^{	ext{II}}(L^4)_2(\text{NO}_3)_2(\text{H}_2\text{O})]$ (7). Hydrogen atoms have been omitted for clarity.

**Fig. S8.** View of the molecular structure of the complex cation of $[\text{Cu}^{	ext{II}}(L^5)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (8). Hydrogen atoms have been omitted for clarity.

**Fig. S9.** View of the molecular structure of $[\text{Cu}^{	ext{II}}(L^5)_2(\text{NO}_3)_2]$ (9). Hydrogen atoms have been omitted for clarity.
**Fig. S10.** View of the molecular structure of the complex cation of [Cu$^{II}$(L$^5$)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ (10). Hydrogen atoms have been omitted for clarity.

**Fig. S11.** View of the molecular structure of [Cu$^{II}$(L$^5$)$_2$Cl$_2$]·MeOH·2H$_2$O·HCl (11). Hydrogen atoms and solvate molecules have been omitted for clarity.

**Fig. S12.** View of the molecular structure of the complex cation of [Fe$^{II}$(L$^5$)$_3$](BF$_4$)$_2$ (12). Hydrogen atoms have been omitted for clarity.
**Fig. S13.** View of the molecular structure of $[\text{Fe}^{II}(L^5)_2(\text{NCS})_2] \cdot 2\text{CHCl}_3$ (13). Hydrogen atoms and solvate molecules have been omitted for clarity.

**Fig. S14.** View of the molecular structure of the complex cation of $[\text{Ru}^{II}(L^5)(\text{bpy})_2](\text{PF}_6)_2$ (14). Hydrogen atoms have been omitted for clarity.

**Fig. S15.** View of the molecular structure of the complex cation of $[\text{Ru}^{II}(L^5)(\text{bpy})_2](\text{PF}_6)_2$ (15). Hydrogen atoms have been omitted for clarity.
**Fig. S16.** View of the molecular structure of [Cu$^{II}$($L^7$)Cl$_2$]·2.5H$_2$O (16). Hydrogen atoms and solvate molecules have been omitted for clarity.

**Fig. S17.** View of the molecular structure of the complex cation of [{Cu$^{II}$($L^8$)}$_4$(NO$_3$)$_4$·8H$_2$O (17). Only two of the four ligands $L^8$ are shown. Hydrogen atoms have been omitted for clarity.
**Fig. S18.** View of the molecular structure of the complex cation of $[\text{Zn}^{II}(\text{L}^9)_2](\text{ClO}_4)_2 \cdot 0.5\text{MeCN}$ (18). Hydrogen atoms have been omitted for clarity.

**Fig. S19.** View of the molecular structure of $[\text{Re}^{III}(\text{L}^{10})(\text{CO})_3\text{Cl}]$ (19). Hydrogen atoms have been omitted for clarity.
**Fig. S20.** View of the molecular structure of $N$-(2-pyridylamino)-2-pyridineamidine (XV).

**Fig. S21.** Hydrogen bonding in the crystal structure of $N$-(2-pyridylamino)-2-pyridineamidine (XV). Selected distances [Å]: N(1)···H–N(12A) 3.007, N(1)···H–N(14A) 3.041, N(2)–H···N(11) 3.011, N(4)–H···N(11) 3.045, N(4)–H···N(5) 2.641, N(4)–H···N(15B) 3.350. Symmetry operations used to generate equivalent atoms: (A) $-x+1, -y+1, -z$; (B) $x, -y+1.5, z+0.5$. 
Fig. S22. View of the molecular structure of 3-(2-pyridyl)-[1,2,4]triazolo[4,3-a]pyridine (L10).

Fig. S23. π–π Stacking in the crystal structure of 3-(2-pyridyl)-[1,2,4]triazolo[4,3-a]pyridine (L10). Selected distances [Å]: \text{cent}<N(1)/C(1)/C(2)/C(3)/C(4)/C(5)>\text{cent}<N(2)/N(3)/N(4)/C(6)/C(7)> 3.387, \text{cent}<N(2)/C(2)/C(21)/C(22)/C(23)/C(24)/C(25)>\text{cent}<N(2)/N(3)/N(4)/C(6)/C(7)> 3.712. Symmetry operations used to generate equivalent atoms: (A) \(-x+1, -y, -z+1\); (B) \(-x+2, -y+2, -z\).
Fig. S24. View of the molecular structure of [Co\textsuperscript{II}(L\textsuperscript{10})\textsubscript{2}(MeOH)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} (20). Hydrogen atoms, except those of the hydroxyl groups of the MeOH co-ligands, have been omitted for clarity. The hydrogen-bonded ClO\textsubscript{4}– counterion is disordered over two positions with site occupancy factors of 0.50 [O(2)–O(4)] and 0.50 [O(5)–O(7)], twirling around the Cl(1)–O(11) bond. Selected distances [Å]: Co(1)–N(1) 2.139(2), Co(1)–N(2) 2.094(2), Co(1)–O(20) 2.093(2), O(3)···O(20) 2.740, O(7A)···O(20A) 2.806. Selected angles [°]: N(1)–Co(1)–N(2) 77.06(7), N(1)–Co(1)–O(20) 91.95(8), N(1)–Co(1)–O(20A) 91.30(8), N(2)–Co(1)–O(20) 88.05(8), N(2)–Co(1)–O(20A) 91.30(8). Symmetry operation used to generate equivalent atoms: (A) –x, –y+2, –z.

Fig. S25. View of the molecular structure of [Ni\textsuperscript{II}(L\textsuperscript{10})\textsubscript{2}(MeOH)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} (21). Hydrogen atoms, except those of the hydroxyl groups of the MeOH co-ligands, have been omitted for clarity. The hydrogen-bonded ClO\textsubscript{4}– counterion is disordered over two positions with site occupancy factors of 0.59 [O(2)–O(4)] and 0.41 [O(5)–O(7)], twirling around the Cl(1)–O(11) bond. Selected distances [Å]: Ni(1)–N(1) 2.108(2), Ni(1)–N(2) 2.070(2), Ni(1)–O(20) 2.052(2), O(4)···O(20) 2.857, O(6A)···O(20A) 2.747. Selected angles [°]: N(1)–Ni(1)–N(2) 79.28(8), N(1)–Ni(1)–O(20) 89.88(9), N(1)–Ni(1)–N(2A) 100.72(8), N(1)–Ni(1)–O(20A) 90.12(9), N(2)–Ni(1)–O(20) 88.81(9), N(2)–Ni(1)–O(20A) 91.19(9). Symmetry operation used to generate equivalent atoms: (A) –x, –y, –z.
**Fig. S26.** View of the molecular structure of [CuII(L10)2(MeOH)2](ClO4)2 (22). Hydrogen atoms, except those of the hydroxyl groups of the MeOH co-ligands, have been omitted for clarity. Selected distances [Å]: Cu(1)–N(1) 2.057(3), Cu(1)–N(2) 1.984(3), Cu(1)–O(1) 2.347(3), O(1)···O(12) 2.844. Selected angles [°]: N(1)–Cu(1)–N(2) 79.62(13), N(1)–Cu(1)–O(1) 90.45(12), N(1)–Cu(1)–N(2A) 100.38(13), N(1)–Cu(1)–O(1A) 89.55(12), N(2)–Cu(1)–O(1) 89.92(12), N(2)–Cu(1)–O(1A) 90.08(12). Symmetry operation used to generate equivalent atoms: (A) –x,