Supplementary Material (ESI) for New Journal of Chemistry
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Supporting Information

Six-coordinate Co^{III} and four-coordinate M^{II} (M = Co, Zn) mixed-valence dimers supported by a deprotonated pyridine amide ligand: magnetism of a $Co^{III}Co^{II}$ complex and C–H···O/Cl/Br interactions

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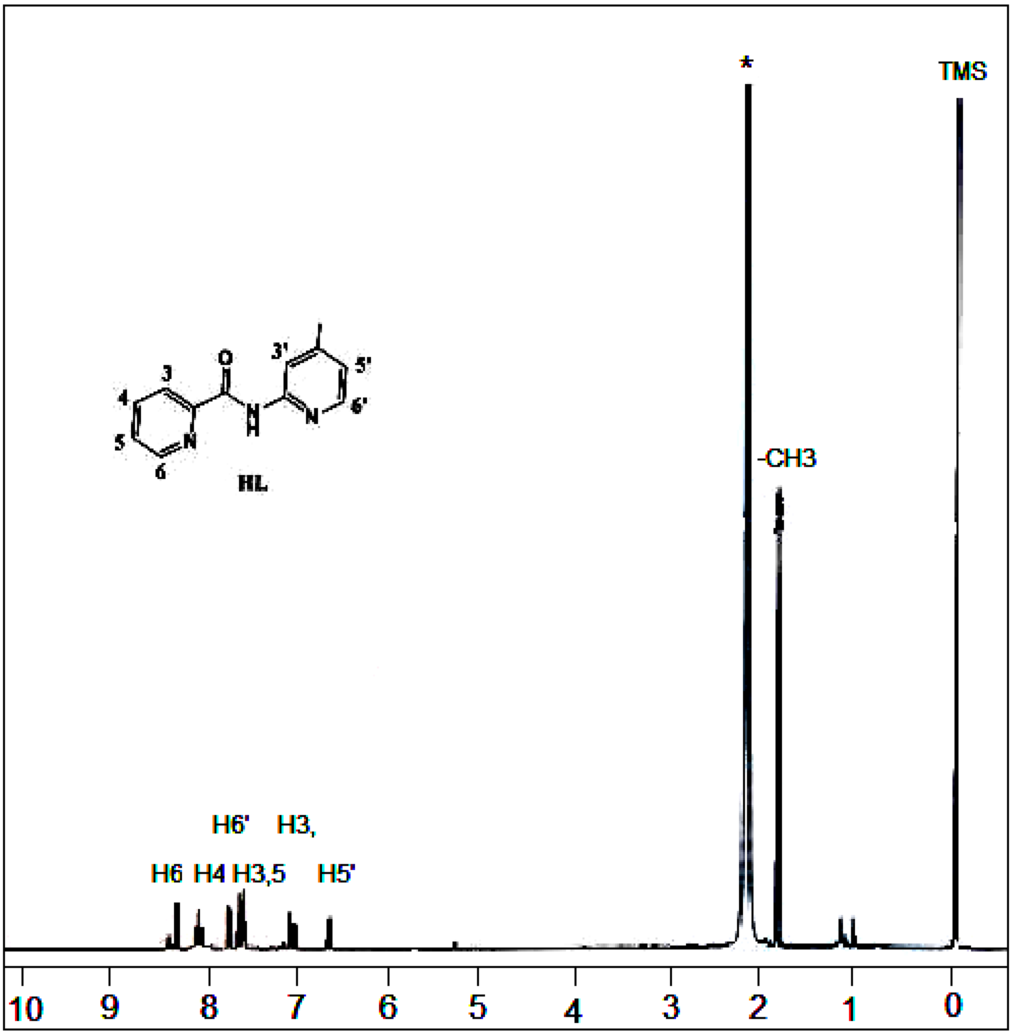
Supplementary Figures



δ/ppm

Fig. S1 ^{1}H NMR spectrum (500 MHz) of $[Co^{III}Zn^{II}(L)_3(Cl)]Cl{\cdot}CH_3OH{\cdot}5H_2O$ (**3**) in CD_3CN at 298 K (water peak is marked by *).

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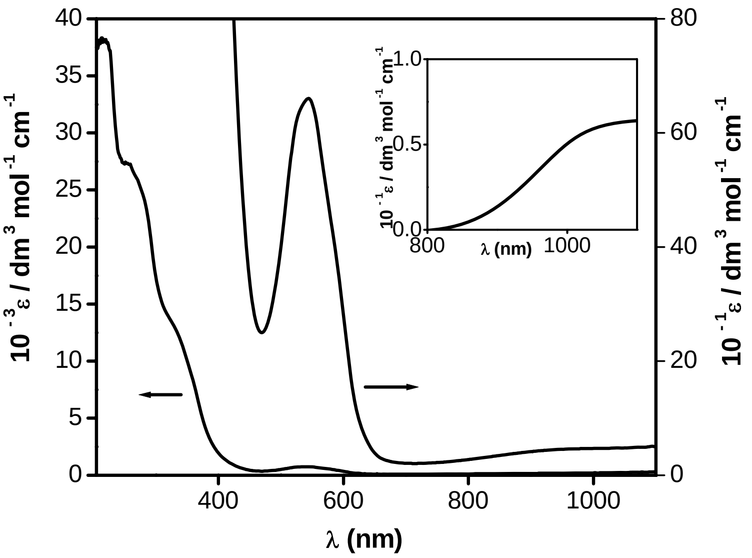

Fig. S2 Absorption spectrum (CH_3CN) of $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**).

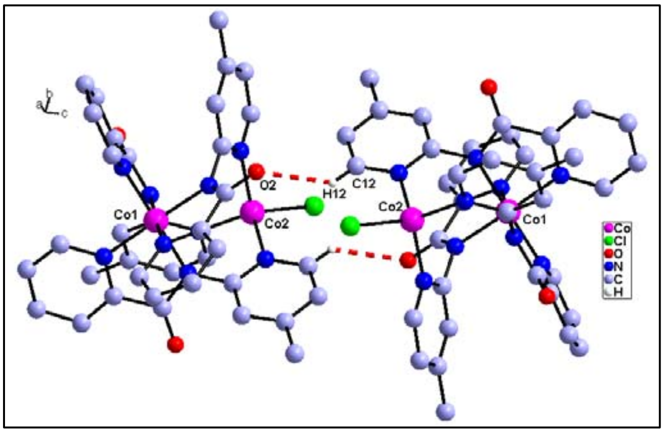

Fig. S3 Perspective view of the formation of a dimer through C–H···O hydrogen-bonding of $[Co^{III,II}_2(L)_3Cl]^+$ unit in $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**). All the hydrogen atoms except those involved in hydrogen-bonding have been omitted for clarity. Dimer is generated by the symmetry operator 2-x, -y, -z.

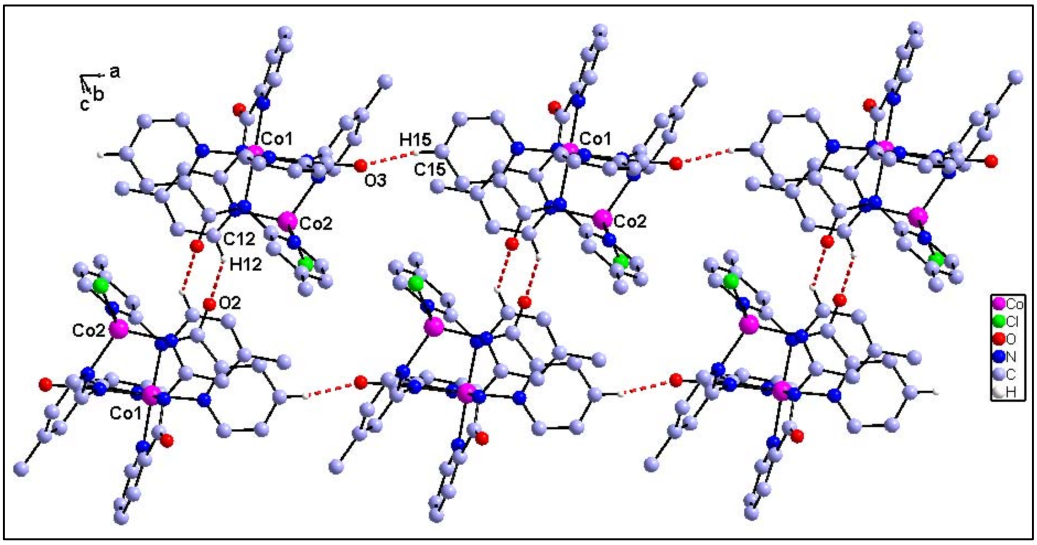

Fig. S4 View of the formation of 1D chain *via* C–H···O hydrogen-bonding of $[Co^{III,II}_2(L)_3(Cl)]^+$ unit in $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**). All the hydrogen atoms except those involved in hydrogen-bonding have been omitted for clarity. ID chain is generated by the symmetry operators 2-x, -y, -z; -1+x, y, z and 1+x, y, z.

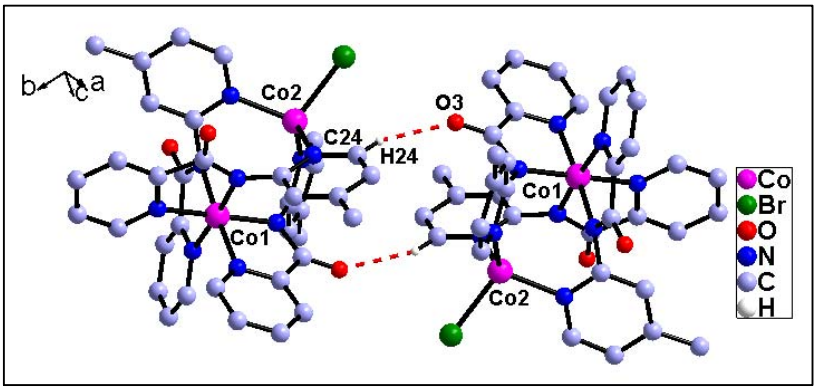

Fig. S5 View of the formation of a dimer through C–H···O hydrogen-bonding of $[Co^{III,II}_2(L)_3(Br)]^+$ unit in $[Co^{III,II}_2(L)_3(Br)]Br{\cdot}CH_3OH$ (**2**). All the hydrogen atoms except those involved in hydrogen-bonding have been omitted for clarity. Dimer is generated by the symmetry operator 2-x, -y, 1-z.

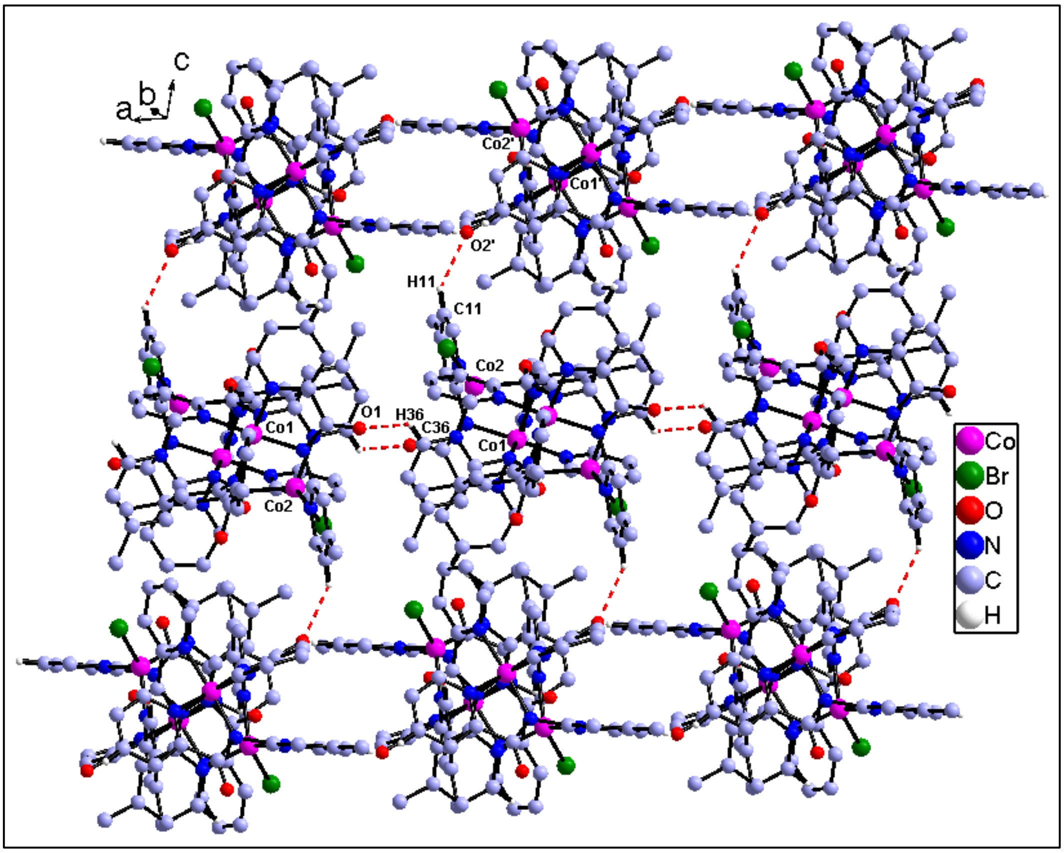

Fig. S6 View of the formation of 2D network *via* C–H···O hydrogen-bonding of $[Co^{III,II}_2(L)_3(Br)]^+$ unit in $[Co^{III,II}_2(L)_3(Br)]Br{\cdot}CH_3OH$ (**2**). All the hydrogen atoms except those involved in hydrogen-bonding have been omitted for clarity. 2D network is generated by the symmetry operator 1-x, 1- y, -z and 1-x, -y, 1-z.

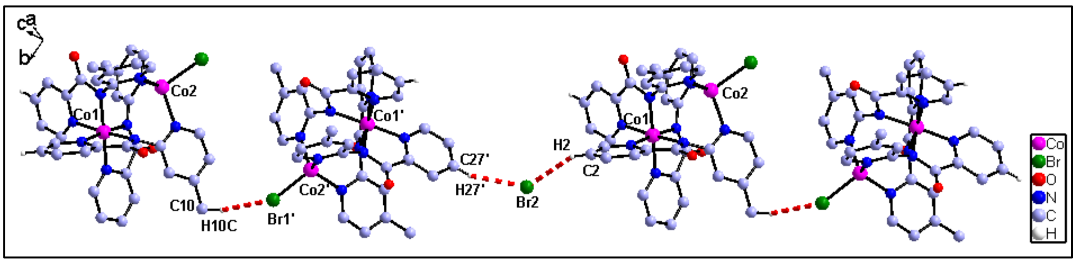

Fig. S7 View of the formation of 1D chain *via* C–H···Br hydrogen-bonding of $[Co^{III,II}_2(L)_3(Br)]^+$ unit in $[Co^{III,II}_2(L)_3(Br)]Br{\cdot}CH_3OH$ (**2**). All the hydrogen atoms except those involved in hydrogen-bonding have been omitted for clarity. 1D chain is generated by the symmetry operators x, y, z; x, 1+y, z; x, -1+y, z; 1+x, y, 1+z and -1+x, y, -1+z.

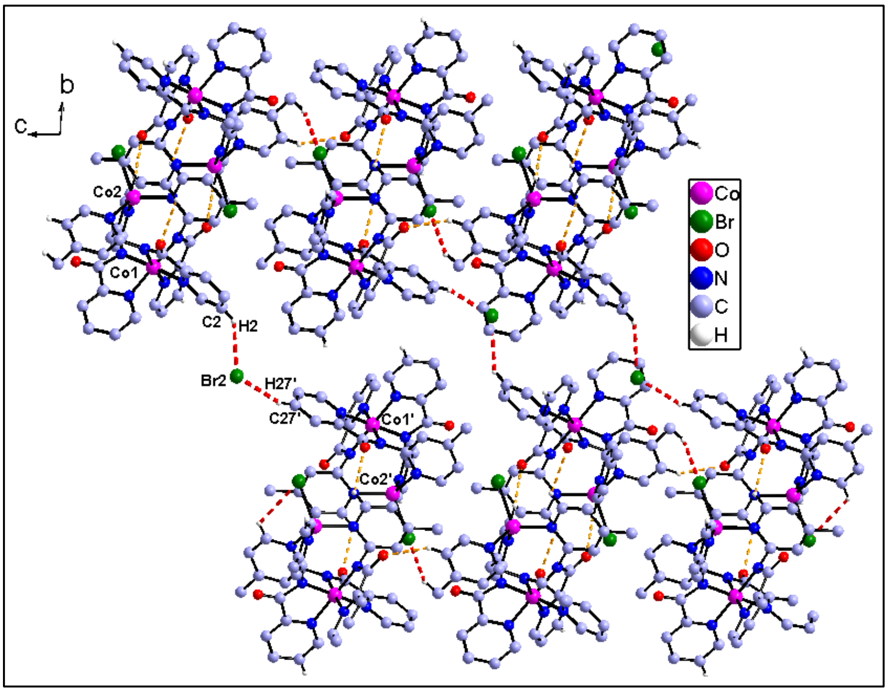

Fig. S8 View (*bc* plane) of the formation of 3D network in $[Co^{III,II}_2(L)_3(Br)]^+$ unit in $[Co^{III,II}_2(L)_3(Br)]Br \cdot CH_3OH$ (**2**) *via* C–H···Br and C–H···O hydrogen-bonding contacts. All the hydrogen atoms except those involved in hydrogen-bonding have been omitted for clarity. 3D network is generated by the symmetry operators x, y, z; 1+x, y, 1+z; -1+x, y, -1+z; 2-x, -y, 1-z; 1-x, -y, 1-z; 1-x, 1- y, -z; x, 1+y, z and x, -1+y, z.

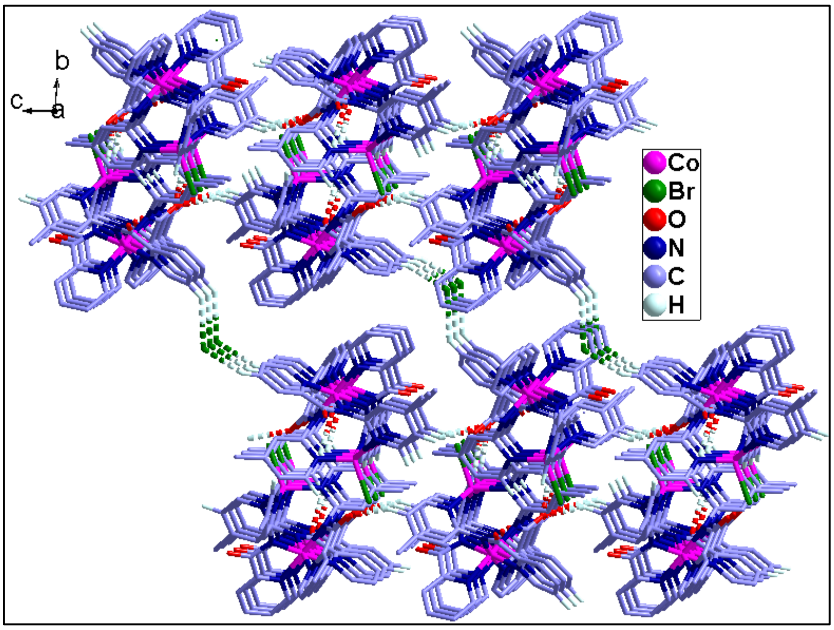

Fig. S9 View (*ab* plane) of the formation of 3D network in $[Co^{III,II}_2(L)_3(Br)]^+$ unit in $[Co^{III,II}_2(L)_3(Br)]Br \cdot CH_3OH$ (**2**) *via* C–H···Br and C–H···O hydrogen-bonding contacts. All the hydrogen atoms except those involved in hydrogen-bonding have been omitted for clarity.

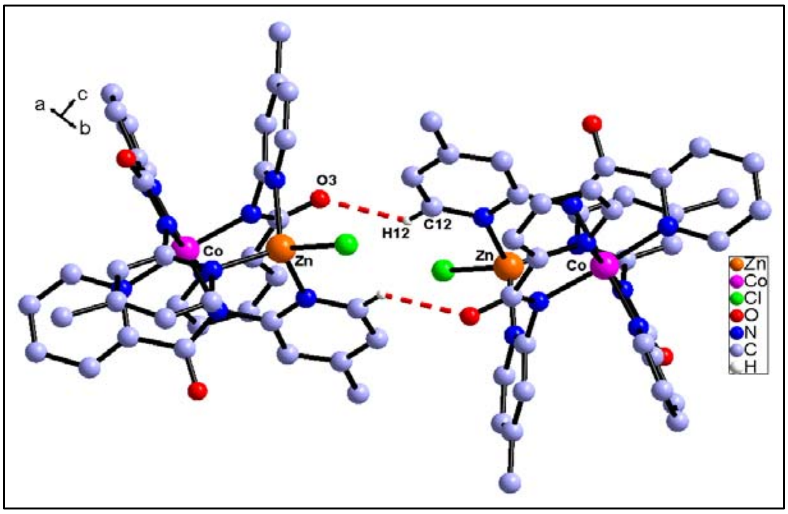

Fig. S10 View of the formation of a dimer through C–H···O hydrogen-bonding of $[Co^{III}Zn^{II}(L)_3(Cl)]^+$ unit in $[Co^{III}Zn^{II}(L)_3(Cl)]Cl·CH_3OH·5H_2O$ (**3**). All the hydrogen atoms except those involved in hydrogen-bonding have been omitted for clarity. Dimer is generated by the symmetry operator 1-x, -y, -z.

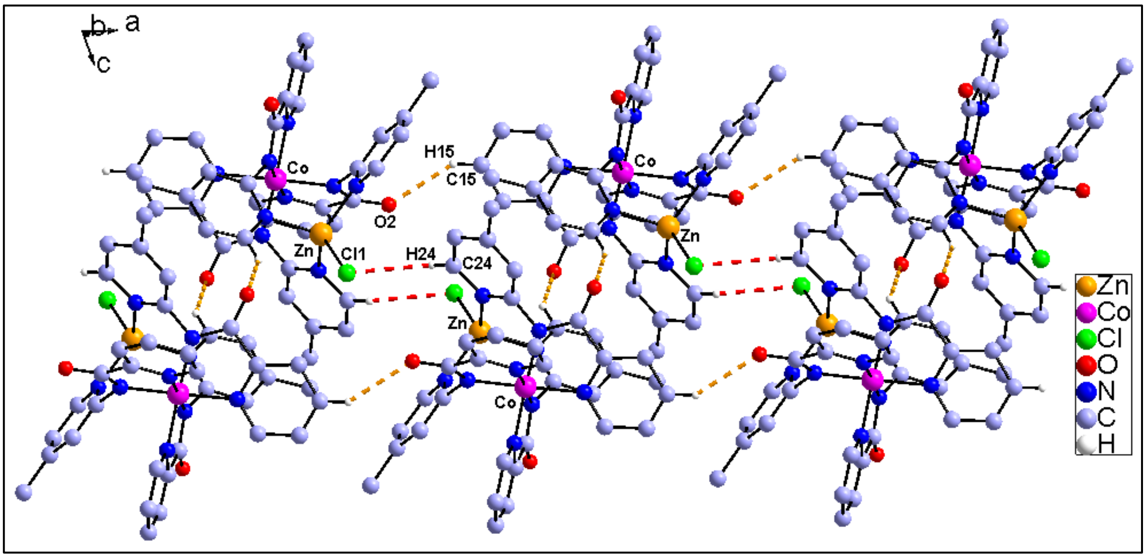

Fig. S11 View (*ac* plane) of the formation of the 1D chain *via* C–H···O and C–H···Cl hydrogen-bonding of $[Co^{III}Zn^{II}(L)_3(Cl)]^+$ unit in $[Co^{III}Zn^{II}(L)_3(Cl)]Cl·CH_3OH·5H_2O$ (**3**). All the hydrogen atoms except those involved in hydrogen-bonding have been omitted for clarity. 1D chain is generated by the symmetry operator 1-x, -y, -z; -1+x, y, z; 1+x, y, z and -x, -y, -z.

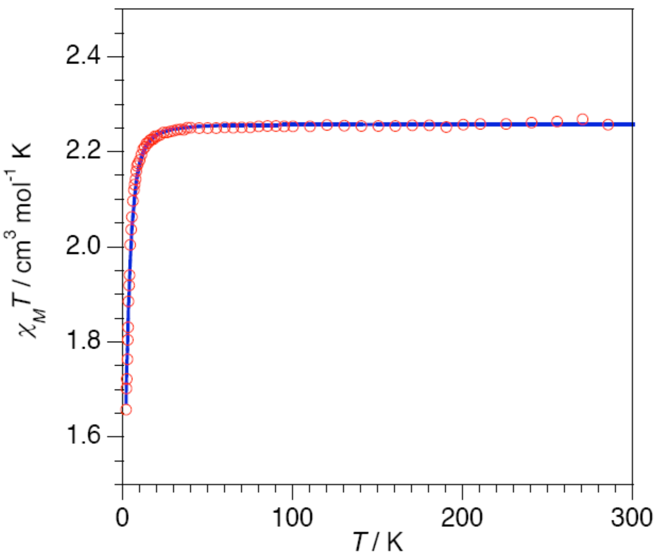

Fig. S12 $\chi_M T$ *vs.* T data and best theoretical plot for $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**).

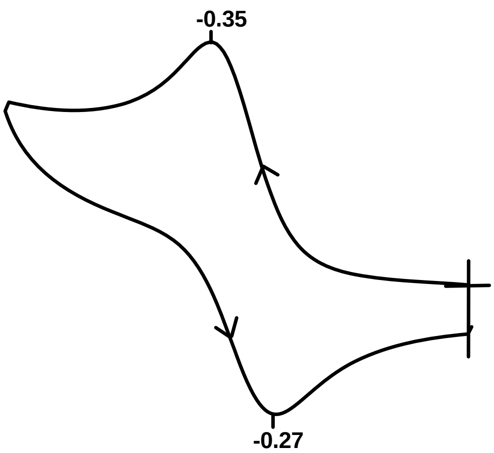

Fig. S13 Cyclic voltammogram (scan rate: 100 mV s^{-1}) of ~1.0 mM solution of $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**) in CH_3CN (~0.1 M in TBAP) at a Pt working electrode. Indicated potentials (in V) are *vs.* SCE.