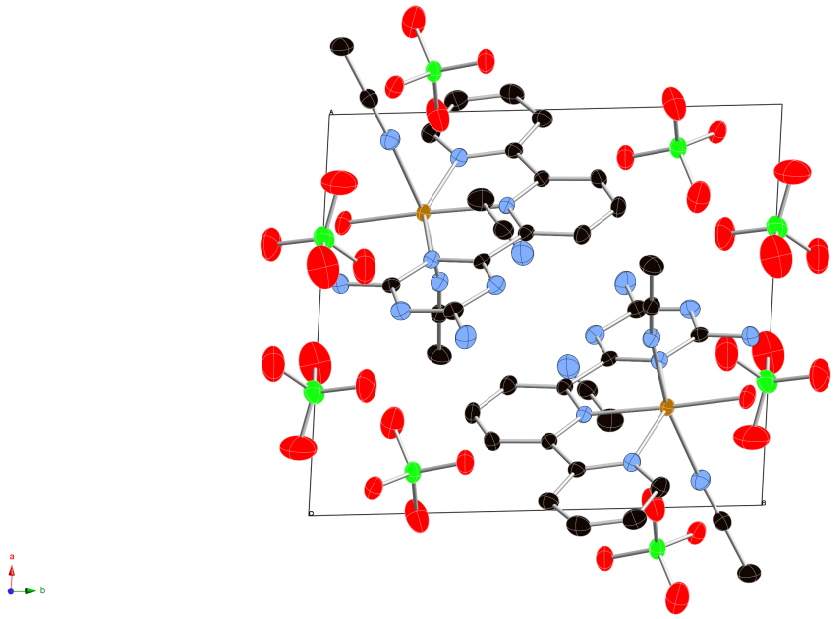

Fig. S1 Projection on the *ab* plane of the structure of **2;** Fe (yellow), C (black), N (blue), O (red) and Cl (green); hydrogen atoms have been omitted for clarity.

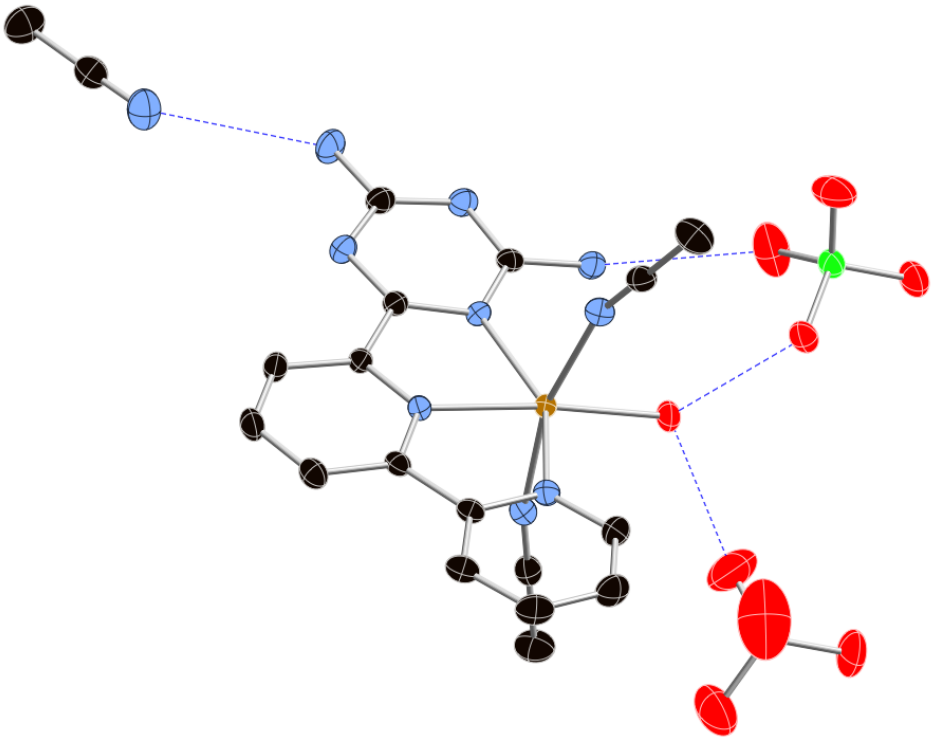

Fig. S2 Hydrogen-bond interactions between $[Fe^{II}(L_1)(CH_3CN)_2(H_2O)]^{2+}$ cations and ClO_4^- counterions in **2**.

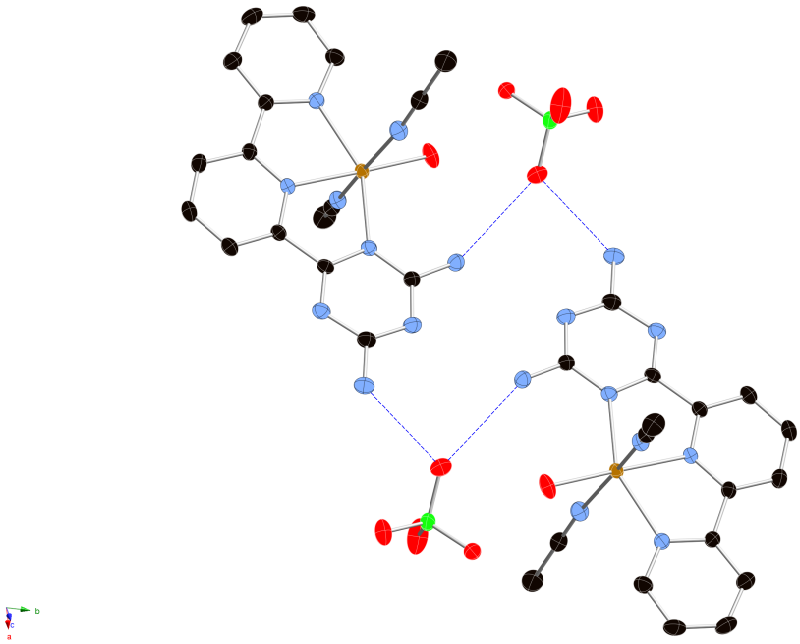

Fig. S3 Hydrogen-bond interactions between pairs of $[Fe^{II}(L_1)(CH_3CN)_2(H_2O)]^{2+}$ cations and ClO_4^- counterions in **2**.

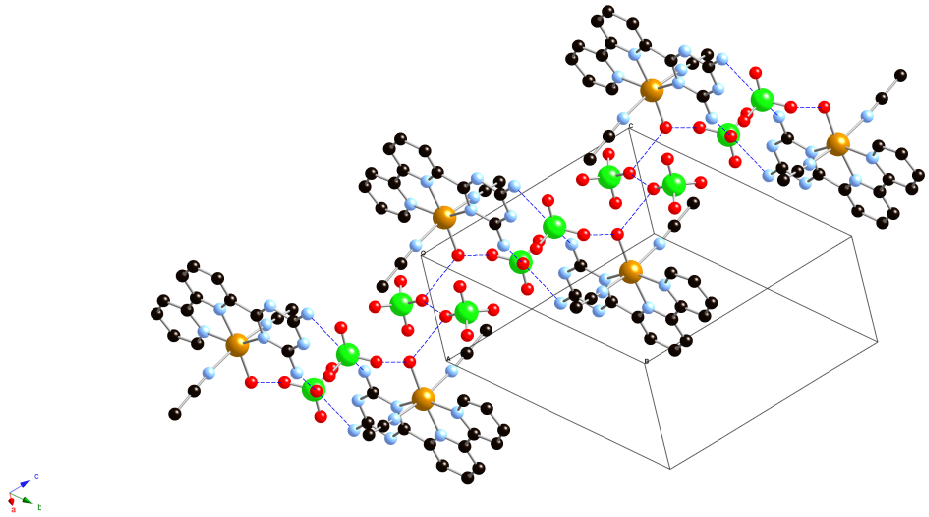

Fig. S4 Chains of $[Fe^{II}(L_1)(CH_3CN)_2(H_2O)]^{2+}$ cations and ClO_4^- counterions connected through hydrogen-bond interactions in **2**.

Two neighbouring $[Fe^{II}(L_1)(CH_3CN)_2(H_2O)]^{2+}$ complexes are linked through two perchlorate anions, which form hydrogen bonds with two amino groups from triazine rings of each complex of the dimer (see Fig. S3). These dimers are linked through another two perchlorate anions forming hydrogen bonds among them and with water molecules from the neighbouring dimers (see Fig. S4). These chains of dimers linked through hydrogen bonds run along the *c* axis.

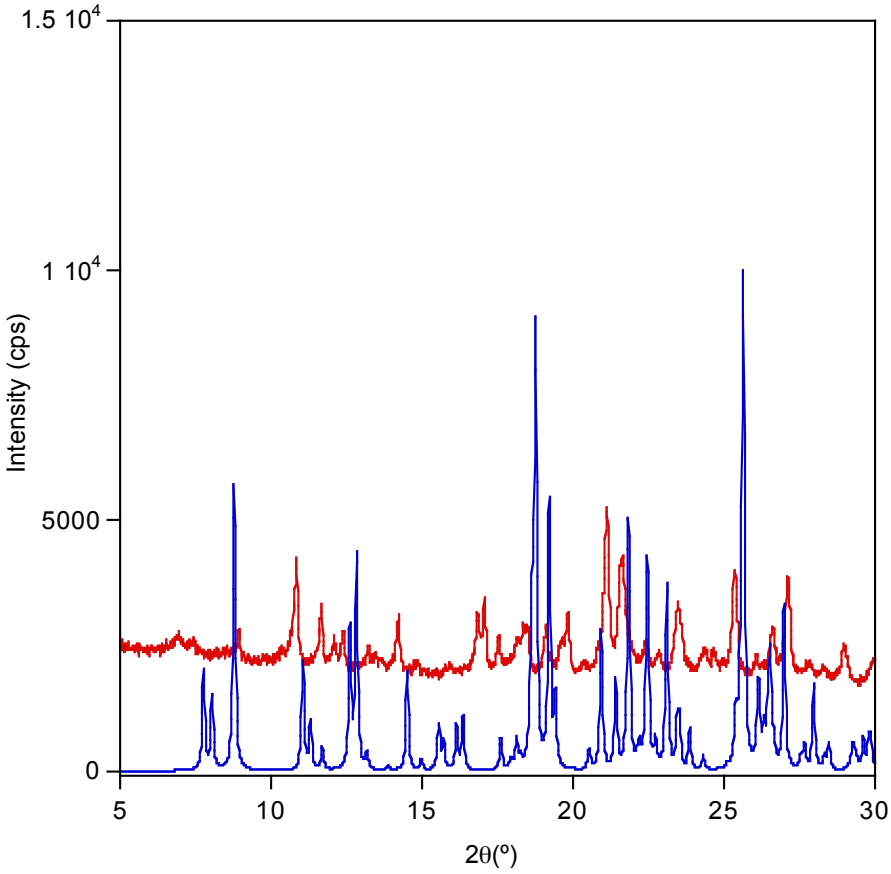

Fig. S5 Powder X-ray diffraction pattern of **2** at room temperature (red) and simulated one from single crystal X-ray diffraction data at 120 K (blue).

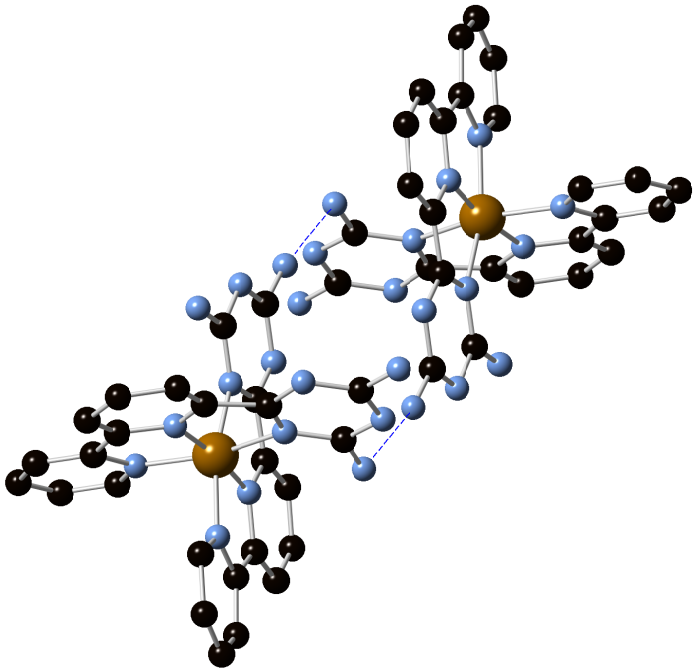

Fig. S6 Dimer of $[Fe^{II}(L_1)_2]^{2+}$ complexes linked through two short contacts between the NH_2 groups from triazine in **3**.