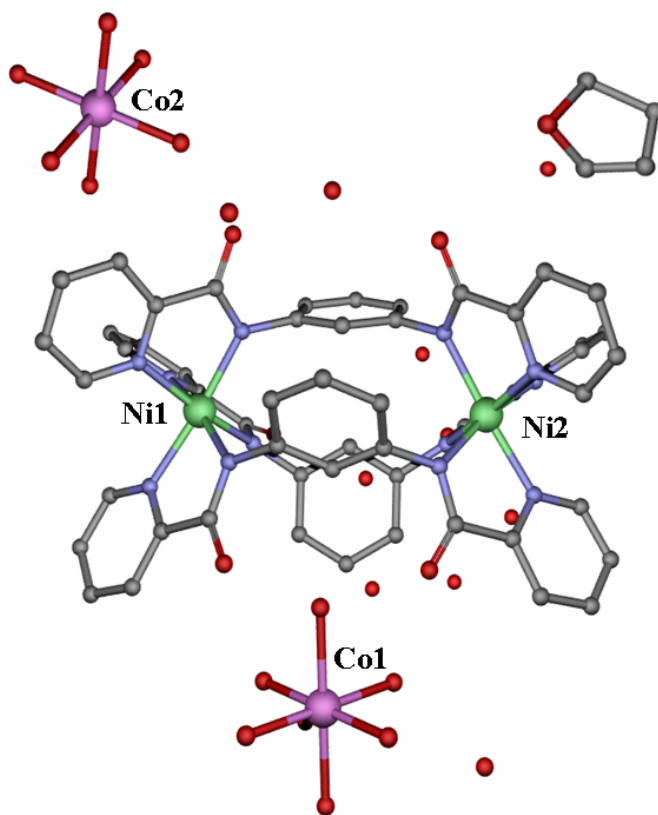


Figure s1



Magnetic properties of 3 and 4

The temperature dependence of the $\chi_M T$ product for **3** (χ_M being the molar susceptibility per Ni₂Co unit) at 300 G is shown in Figure S2.

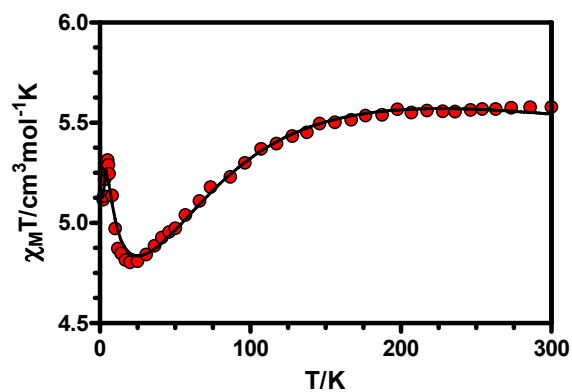


Figure S2.- Thermal dependence of $\chi_M T$ for **3** at 2 K. The solid line represents the calculated curve fit.

The room temperature $\chi_M T$ value of $5.57 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is much higher than the expected spin-only value for two Ni(II) ions with $g = 2$, $S = 1$ and one Co(II) ion with $g = 2$ and $S = 3/2$ ($3.875 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$), which is due to the spin-orbit coupling effect of the octahedral Co(II) ions. However, the $\chi_M T$ value is close to the sum of the experimental values reported for Ni₂ dinuclear complexes and Co(II) complexes. The $\chi_M T$ vs T plot shows that the $\chi_M T$ decreases continuously upon cooling and reach a minimum of $4.80 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 20 K. This behaviour is mainly attributed to the depopulation of the spin-orbit coupling excited sublevels of the octahedral Co(II) ion. Below 20 K, the $\chi_M T$ product increases to a maximum of $5.31 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5 K and then decreases to $5.11 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2K. This increase is due to the ferromagnetic interaction between the Ni(II) ions through spin-polarisation whereas the sharp decrease below 4 K can be attributed to both ZFS of the $S = 2$ ground state of the Ni₂ unit and/or intermolecular interactions. The $\chi_M T$ data were fitted to the to the sum of the expressions for a mononuclear octahedral Co(II) complex¹⁹ and a dinuclear Ni₂ complex (there is not any analytical expression that simultaneously accounts for both the spin-orbit coupling and ZFS promoted by the octahedral distortion). The best fitting parameters were: $J_{\text{NiNi}} = 3.6(4) \text{ cm}^{-1}$, $\lambda = -156(7) \text{ cm}^{-1}$, $A = 1.02$, $g_{\text{Ni}} = 2.33(3)$ and $\theta = -0.26(5) \text{ K}$, where λ is the spin-orbit coupling parameter, which is -170 cm^{-1} for the free ion and A is a measure of the crystal field strength due to interelectronic repulsions. A θ parameter was included to account for the intermolecular interactions (this parameter also include the ZFS effects). The J_{NiNi} values is similar to that observed for compound **2**, whereas the λ and A values for the Co(II) ion are in line with those observed for other distorted octahedral Co(II) complexes. In view of this, it seems that the existence of full-deprotonated or semi-deprotonated ligands in the Ni₂ complexes has not any significant influence on the magnetic properties of these complexes.

As expected, the magnetic behaviour of **4**, which is shown in Figure S3 in the form $\chi_M T$ vs T (χ_M being the magnetic susceptibility per Ni₂ unit) is very similar to those of compounds **2** and **3** and is indicative of intradinuclear Ni₂ ferromagnetic interaction with very small intermolecular exchange interactions and/or ZFS effects of the triplet ground state. In fact, the isothermal magnetisation for **4** at 2 K match well with the Brillouin function for an isolated quintuplet state with $g = 2.1$. The simulation of the magnetic data led to $J = 2.9(3) \text{ cm}^{-1}$, $g = 2.17(8)$, $D_{\text{Ni}} = -0.42(4)$ and $zJ' = -0.09(1) \text{ cm}^{-1}$.

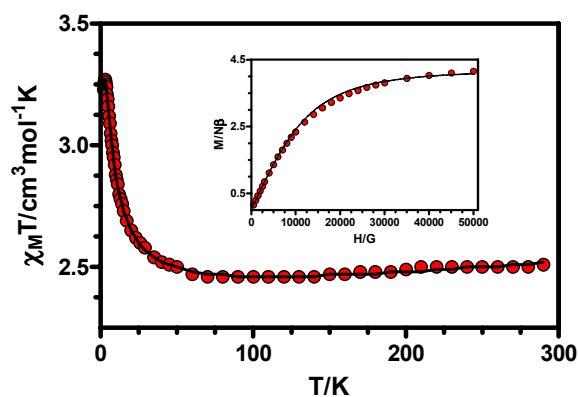


Figure S3.- Temperature dependence of $\chi_M T$ in **4**. The circles and lines represent, respectively, the experimental data and the simulation using the parameters obtained in the fit process. The inset shows the field dependence of the magnetisation for **4** at 2 K (the solid line represents the Brillouin function for $S = 2$).