A high spin molecular square based on square pyramidal Co^{II} and tetrahedral Mn^{II} centers: $[\{\mathrm{Mn^{II}Cl_2}\}_2\{\mathrm{Co^{II}(triphos)(CN)_2}\}_2]$†

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A high spin molecular square of square pyramidal Co^{II} and tetrahedral Mn^{II} corners exhibiting an overall S = 4 ground state has been crystallized and its magnetic properties investigated.

One of the current themes in the field of coordination chemistry is the preparation of polynuclear metal complexes with interesting photophysical, electronic, and magnetic properties.[1,2] Among the most well-studied molecules in the area of controlled self-assembly reactions of metal ions is the molecular square, whose formation is favored both enthalpically and entropically.[3–9] Most of the linkers that have been used in the cyclization reactions that lead to molecular squares and related geometries are based on nitrogen heterocyclic ligands,[10–12] with a notable exception being the cyanide ligand which has been used to prepare molecular squares from octahedral or square planar metal ion building blocks.[2–5,7,9]

One of the reasons for the interest in cyanide-based clusters is that the two atom linkage of cyanide (~5.0 Å) provides an efficient pathway for magnetic coupling which can lead to molecules with high spin ground states. Since the geometry of each metal center as well as the linking group exerts an influence on the overall magnetic behavior of the clusters, an interesting issue to explore is the control and variation of geometries within the square ensemble. Given our recent success in preparing a family of cubic clusters using triphos (1,1,1-tris(diphenylphosphinomethyl)-ethane) as a capping ligand for the Re^{II} ion,[13,14] we have sought to employ other triphos containing metal precursors to systematically prepare additional cluster topologies in order evaluate their magnetic properties. Herein we report the use of the five-coordinate square pyramidal complex, [Co^{II}(triphos)(CN)$_2$], first synthesized by Rupp *et al.*,[15] as a starting material for the preparation of a molecular square consisting of distorted square pyramidal Co^{II} and tetrahedral Mn^{II} corners.

The reaction of [Co(triphos)(CN)$_2$] and MnCl$_2$ in CH$_2$Cl$_2$/EtOH produces a greenish-gray crystalline solid, **1**, in good yield.‡ A single crystal X-ray analysis of **1** revealed the identity of the product as $[\{\mathrm{Mn^{II}Cl_2}\}_2\{\mathrm{Co^{II}(triphos)(CN)_2}\}_2]\cdot 4\mathrm{CH_2Cl_2}$, a distorted molecular square with alternating Co^{II} and Mn^{II} ions located at the vertices spanned by bridging cyanide ligands (Fig. 1).§ The Co^{II} sites remain pentacoordinate in the complex, and the Mn^{II} sites are in distorted tetrahedral environments consisting of two cyano-nitrogen atoms and two chloride ions. The net charge on the cluster is zero. The molecule crystallizes on an inversion center, such that the asymmetric unit is composed of one-half of a square molecule. The distorted tetrahedral geometry at the Mn^{II} site is a result of the steric demand of the triphos ligand, as previously observed for molecular cubes,[13,14] and other structures.[16,17] The most severe distortions of the overall structure occur at the C–Co–C (84.87(17)°) and N–Mn–N (103.16(14)°) angles.

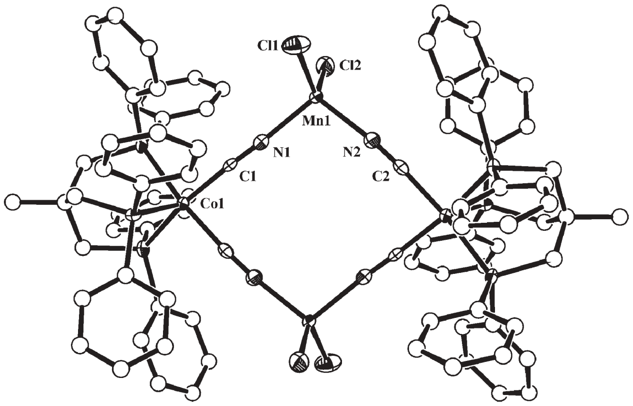

Fig. 1 Thermal ellipsoid plot of $[\{\mathrm{MnCl_2}\}_2\{\mathrm{Co(triphos)(CN)_2}\}_2]$ (**1**). Carbons atoms of the triphos ligand are shown as spheres of arbitrary radius and hydrogen atoms have been omitted for the sake of clarity. Ellipsoids are projected at the 50% probability level.

Infrared spectroscopy performed on a crushed, polycrystalline sample of **1** revealed the expected shift of the $\nu_{C\equiv N}$ stretches to higher energies, due to the adoption of a linear bridging cyanide mode.[17] The $\nu_{C\equiv N}$ band appears at 2128 cm^{-1} which is shifted by +32 cm^{-1} as compared to the starting material (2096 cm^{-1}).

Molecular squares have been reported for a variety of metal–cyanide building blocks,[3–9] the most important example of which in the present context is the S = 2 Fe$_2$Cu$_2$ square reported by Oshio *et al.*[4] Squares are attractive in magnetic studies because the overall shape of the cluster is anisotropic (*i.e.*, it is a flat molecule) hence the cancellation of the local anisotropies of the ions observed in other high symmetry metal–cyanide clusters is expected to be reduced.[18,19] The magnetic properties of **1** were investigated by performing temperature dependent magnetic susceptibility measurements in the range T = 2–300 K (Fig. 2) on a crushed polycrystalline sample of **1** whose purity had been confirmed by elemental analysis.¶ The data reveal an initial decrease in the value of χT vs. T response, consistent with local antiferromagnetic coupling between the S = 1/2 Co^{II} and S = 5/2 Mn^{II} ions, until $T \cong 65$ K, at which temperature the value abruptly increases to reach a maximum of 9.96 emu K mol^{-1} (8.92 μ_B) at 6 K. At 300 K

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† Electronic supplementary information (ESI) available: Temperature dependent magnetic susceptibility data on the complex Co(triphos)(CN)$_2$. See http://www.rsc.org/suppdata/cc/b4/b415168b/

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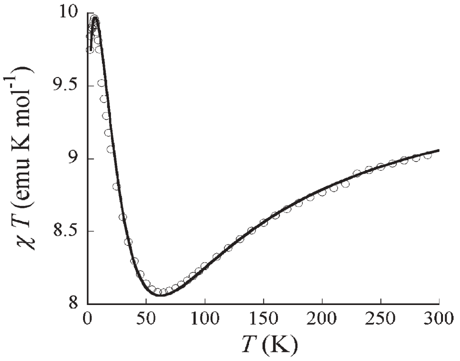

Fig. 2 Temperature dependent magnetic susceptibility data for **1** collected in the temperature range of 1.8–300 K at 0.1 T. The solid line represents the MAGPACK model for the exchange interaction between the Co^{II} and Mn^{II} ions with $J = -9.0$ cm^{-1} and $g = 2.02$.

the χT product is 9.04 emu K mol^{-1} (8.50 μ_B), in accord with the expected value of 9.59 emu K mol^{-1} (8.76 μ_B) from the sum of two $S = 5/2$ Mn^{II} ions and the value for the $S = 1/2$ Co^{II} parent complex (0.42 emu K mol^{-1}, 1.83 μ_B).|| Field dependent magnetization data collected at 1.8 K in the range of 0–7 T reveal the onset of saturation at ~2.5 T, reaching a value of 8.31 μ_B at 7.0 T. Comparison with the Brillouin function for an $S = 4$ paramagnet clearly indicates that the ground state of the molecule from AF coupling of the Co^{II} and Mn^{II} metal ions is $S = 4$ (Fig. 3). An acceptable model for the temperature dependent magnetic susceptibility of **1** was achieved using MAGPACK,[20] by applying the following Hamiltonian for the spin interactions in the cluster and the mean field approximation to account for the low temperature behavior.

$$\hat{H} = -2J\left(\hat{S}_{Co(1)} + \hat{S}_{Co}(2)\right)\cdot\left(\hat{S}_{Mn(1)} + \hat{S}_{Mn(2)}\right)$$

The geometry (distorted square pyramidal) and strong ligand field of the Co^{II} sites in the molecule quenches the orbital contribution, thus the Hamiltonian and model need only depend on the spin operators for the Co^{II} and Mn^{II} ions. The model yielded values of $J = -9.0$ cm^{-1}, $g = 2.02$, and $zj' = -0.01$ cm^{-1} indicating an antiferromagnetic interaction between the Co and Mn centers. AC susceptibility experiments performed on **1** showed no evidence for magnetic ordering or slow paramagnetic relaxation.

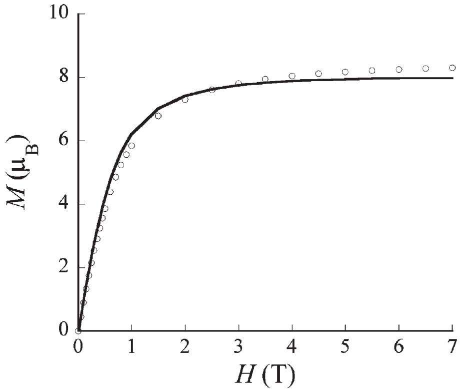

Fig. 3 Field dependent magnetization data for 1 collected at 1.8 K. The solid line shows the Brillouin function for an $S = 4$ paramagnet.

The present result supports our hypothesis that the synthetic methodology developed for the Re^{II} precursor $[Et_4N]$-$[Re(triphos)(CN)_3]$ to prepare high spin clusters can be employed for a variety of metal–cyanide triphos complexes. As was observed in the case of the Re^{II} clusters, the triphos ligand exerts considerable steric demand on neighboring metal ion sites, the consequence of which is a tetrahedral geometry for the other vertices. The bulk of the triphos ligand also serves to insulate the clusters from each other, which prevents long range magnetic ordering through dipolar interactions. This approach to forming magnetic squares based on the Co precursor is not limited to Mn(II) ions, and, indeed, a whole family of compounds of general formula $[\{MCl_2\}_2\{Co(triphos)(CN)_2\}_2]$ (M = Mn, Fe, Co, Ni, Zn) is now available, the details of which are forthcoming in a future report.

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Notes and references

‡ Synthesis of $\{[Co(triphos)(CN)_2]_2[MnCl_2]_2\}$(**1**): A maroon solution of $Co(triphos)(CN)_2$ (100 mg, 0.136 mmol) dissolved in 30 mL of dichloromethane was slowly layered with a solution of $MnCl_2$ (0.034, 0.272 mmol) dissolved in 30 mL of ethanol. The mixture was allowed to stand undisturbed for 3–4 days. Dark green crystals of **1** were obtained by filtration and washed with copious amounts of ethanol. Yield 0.047 g, 40%.

§ Crystal data for **1**·4 CH_2Cl_2: $C_{90}H_{86}N_4Cl_{12}P_6Co_2Mn_2$ $M = 2062.59$, monoclinic, $P2_1/n$ (No. 14), $a = 14.079(3)$ Å, $b = 16.444(4)$ Å, $c = 19.995(5)$ Å, $\beta = 90.129(4)°$, $V = 4629(8)$ Å^3, $Z = 2$, $\rho_c = 1.480$ g cm^{-3}, $\mu = 1.116$ mm^{-1}, 45463 reflections (10446 unique, $R_{int} = 0.1465$) with $2\theta = 54.96°$, 502 variables, $R = 0.0697$, $R_w(F_o^2) = 0.1566$ [5398 data, $I > 2\theta(I)$], GOF = 0.892. Data were measured at $T = 110(2)$ K on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα ($\lambda_\alpha = 0.71073$ Å) radiation. The structure was solved and refined using SHELX97 (Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997) with the graphical interface X-SEED (Barbour, L. J. 1999 X-Seed, Graphical interface to SHELXL-97 and POV-Ray). The option SQUEEZE in PLATON (van der Sluis & Spek, 1990; Spek, 2001) was used to eliminate the contribution of the electron density in the solvent region from the intensity data. The use of SQUEEZE produced better refinement results, and the solvent-free model was employed for the final refinement. Hydrogen atoms were placed in calculated positions and refined with displacement parameters that are 1.2 or 1.5 times that of the heavy atoms to which they were bonded. CCDC 252047. See http://www.rsc.org/suppdata/cc/b4/b415168b/ for crystallographic files in .cif format.

¶ Anal. Calcd. for **1**, $C_{86}H_{78}Cl_4N_4P_6Co_2Mn_2$: C, 59.95; H, 4.56; N, 3.25; Cl, 8.23. Found: C, 59.59; H, 4.63; N, 3.16; Cl, 8.07.

|| The magnetic moment of $Co(triphos)(CN)_2$ at 20 °C was reported to be 1.80 μ_B (0.41 emu K mol^{-1}).[15] Our temperature dependent susceptibility studies (see ESI†), determined the value to be slightly higher at 0.42 emu K mol^{-1} (1.83 μ_B).

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