[MS35-P03] Azido-Bridging Cobalt(II) Systems: Crystal Structures and Magnetic Properties.

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The synthesis and rational design of polynuclear coordination compounds is still a challenge in magneto-chemistry for developing of new functional molecule-based materials. The threeatom azido bridging ligand is one of the most extensively investigated building block due to its versatility to produce polynuclear 3d coordination compounds of different dimensionalities: from molecular to 3D systems [1]. In addition the azido ligand is able to coordinate in different bridging modes. The most common are μ 1,1 (end-on, EO), which usually promotes ferromagnetic, F, interactions, and the μ 1,3 (end-to-end, EE), which typically promotes anti-ferromagnetic, AF, interactions, further tri-and tetra-dentate bridging modes have been observed. Compared to azido complexes of Cu(II), Ni(II) or Mn(II), the number of reported polynuclear Co(II) azido complexes is relative small, mainly caused by synthetic problems to obtain good quality single crystals. Following our work in this field we report a comparative magneto-structural study of a series of azido-bridged Co(II) complexes

with N-donor containing co-ligands, mainly pyridine derivative ligands [2-7]: A tetranuclear Co-cluster with defective dicubane structure was found for $[Co_4(N_3)_8(4,5-diazafuoren-9$ one),]. Polymeric 1D systems were observed for $[Co(N_3),(pyridine),(H_2O)]n$, $[Co(N_3),(3,5 [utidine)_2]_n$, $[Co(N_3)_2(4ethylpyridine)_2]_n$ $[Co(N_3)_2(3-picoline)_2]_n$, $[Co(N_3)_2(pyridine-4$ $carbaldoxime)_{2}$ and $[Co_{3}(N_{3})_{4}(4ethylpyridine)_{10}]$ $_{n}$ (PF₆)_{2n}. In addition to EE azido-bridges also alternating bridging sequences, like di-EO/ di-EE, di-EO/di-EO/di-EE, and di-EO/EE/EE exists in these chains compounds; the latter di-EO/EE/EE sequence induces a topological FERRI-magnetic coupling of the Co(II) centers. Two-dimensional EE-azido only bridged square layers systems were found in the crystal structures of $[Co(N_3)_2(4-acetylpyridine)_2]_n$ $[Co(N_3)_2(2,5dimethylpyrazine)]_n$ and $[Co(N_3)_2(2$ aminopyrimidine)], A unusual 3D Co-azidosublattice exists in $[Co_2(N_3)_4(hmt)(H_2O)]n$ (hmt = hexamethylenetetramine) network structure.

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