

# Novel Dinucleating Ligand Systems Containing Two Adjacent Coordination Compartments of the Potential Triamidoamine-Type – Nickel(II) and Cobalt(II) Coordination Chemistry

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The preparation of novel dinucleating pyrazolate ligands  $H_5L^3$  -  $H_5L^8$  carrying chelating side arms with appending secondary amine functions is reported. Following different synthetic routes, either  $CH_2CF_3$ ,  $C_6H_2F_3$ , or  $C_6F_5$  moieties can be introduced as substituents at the terminal nitrogen atoms. These systems are reminiscent of two coupled coordination compartments of the potential triamidoamine-type. Crystallographic analyses of a series of bimetallic complexes of the  $CH_2CF_3$ -substituted ligand  $H_5L^4$  with  $NiCl_2$  and  $CoCl_2$  reveal manifold coordination modes in the solid state, resulting from the facile detachment of a single or several N-donor sites from the metal centers. Coordination number sets  $\{4/6\}$  (in  $H_5L^4Co_2Cl_4$ ) and  $\{5/6\}$  (in  $H_4L^4Ni_2Cl_3$ ,  $H_4L^4Co_2Cl_3$  and  $H_5L^4Ni_2Cl_4$ ) are thus observed. In the non-deprotonated  $H_5L$ -type systems the remaining protons are found to be scavenged by a pyrazolate-N (in  $H_5L^4Ni_2Cl_4$ ) or an amine function of a ligand side arm (in  $H_5L^4Co_2Cl_4$ ).