

Synthesis and Characterization of New Cyano-Bridged Oligonuclear Complexes

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The main synthetic route leading to heteropolynuclear cyano-bridged complexes consists in the employment of the stable cyanometallate anions as ligands toward either fully solvated metal ions, or toward metal complexes, which have at least one coordination site occupied by a weakly binding ligand that can be easily replaced.

The reaction between $[M(CN)_6]^{3-}$ ($M^{III} = Cr, Fe, Co$) and $[Mn(MAC)X_2]$ (MAC = macrocyclic ligands, $X = H_2O, NCS^-$) affords a series of cyano-bridged trinuclear complexes. The cryomagnetic properties of the Cr^{III} derivatives were investigated, revealing a new case of irregular spin-state structure.

A series of binuclear 3d-4f complexes $\{(H_2O)_8Ln-NC-Fe(CN)_5\} \cdot nhmt$ ($Ln(III) = La, Pr, Sm, Gd, Dy, Ho$; hmt = hexamethylenetetramine; $n = 1, 2$) has been synthesized and crystallographically characterized. They exhibit two structural types governed by the size of the assembling 4f cations. Such complexes are suitable models for the study of the 3d-4f exchange interactions mediated by the cyano bridge.

Keywords: cyanide complexes, lanthanides, magnetism