A Theoretical Study on the Existence and Structures of Some Hypothetical First-Row Transition-Metal *M*(NCN) Compounds

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The family of quasi-binary cyanamides/carbodiimides of general formula *M*(NCN) containing divalent 3*d* transition metals (*M* = Mn, Fe, Co, Ni and Cu) has been studied by density-functional means; until now, such light transition-metal compounds have not yet been prepared. Twenty-eight structural models have been considered based on known compounds having NCN^{2-} and other triatomic anionic entities (*e. g.*, thiocyanates). After performing LDA geometry optimizations, the relative energetic orderings are interpreted in terms of geometrical factors such as molar volumes and effective coordination numbers; dense structures with octahedral metal coordinations and high-spin electronic configurations are to be expected, especially for the earlier metals (Mn and Fe). Based on GGA total-energy calculations, there is a chance to synthesize these enthalpically unstable compounds, not from the elements but *via* appropriate exchange reactions employing fairly stable cyanamide/carbodiimide precursors and yielding stable or volatile metal halides which can be removed from the chemical equilibria.

Key words: Light Transition Metals, Cyanamides/Carbodiimides, Geometry Optimization, Density-Functional Theory, Phase Prediction