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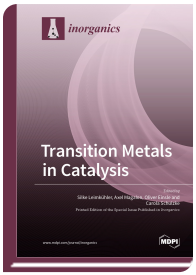
Transition Metals in Catalysis



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Iron–sulfur (FeS) centers are essential protein cofactors in all forms of life. They are involved in many key biological processes. In particular, Fe-S centers not only serve as enzyme cofactors in catalysis and electron transfer, they are also indispensable for the biosynthesis of complex metal-containing cofactors. Among these cofactors are the molybdenum (Moco) and tungsten (Wco) cofactors. Both Moco/Wco biosynthesis and Fe-S cluster assembly are highly conserved among all kingdoms of life. After formation, Fe-S clusters are transferred to carrier proteins, which insert them into recipient apo-proteins. Moco/Wco cofactors are composed of a tricyclic pterin compound, with the metal coordinated to its unique dithiolene group. Moco/Wco biosynthesis starts with an Fe-S cluster-dependent step involving radical/S-adenosylmethionine (SAM) chemistry. The current lack of knowledge of the connection of the assembly/biosynthesis of complex metal-containing cofactors is due to the sheer complexity of their synthesis with regard to both the (genetic) regulation and (chemical) metal center assembly. Studies on these metal-cofactors/cofactor-containing enzymes are important for understanding fundamental cellular processes. They will also provide a comprehensive view of the complex biosynthesis and the catalytic mechanism of metalloenzymes that underlie metal-related human diseases.

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