

2-Diphenylphosphino-phenol as a Ligand for Mono- and Poly-Nuclear Complexes of Manganese, Cobalt, Nickel, Zinc, and Cadmium

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2-Diphenylphosphino-phenol was chosen as an ambivalent (hard/soft) chelating ligand for biologically important first row transition metals. The expected mode of complexation is relevant to trapping of metal ions in humic acids and related environmental ion exchange systems with phenolate functions. The 1:2 complex with nickel(II) is known to have a standard mononuclear square-planar structure, and experimental evidence suggests that the new cobalt(II) complex is analogous. By contrast, zinc and cadmium were found to give novel trinuclear complexes $[M_3(2\text{-Ph}_2\text{P-C}_6\text{H}_4\text{O})_6]$, $M = \text{Zn, Cd}$. In a chain of three metal atoms, the octahedrally coordinated central atom resides on a center of inversion and is solely oxygen-bound $[\text{MO}_6]$, while the two peripheral metal atoms are in a mixed coordination environment $[\text{fac-MO}_3\text{P}_3]$. The analogous manganese(II) complex crystallizes as a net trihydrate, where two different trinuclear units are present in the lattice. One is of a new type and represents a centrosymmetrical hexahydrate $[\text{Mn}_3(2\text{-Ph}_2\text{P-C}_6\text{H}_4\text{O})_6(\text{OH}_2)_6]$. The central part is an octahedral $[\text{Mn}(\text{OH}_2)_6]^{2+}$ dication, which is hydrogen-bonded to two $[\text{Mn}(2\text{-Ph}_2\text{P-C}_6\text{H}_4\text{O})_3]^-$ anions. The nickel(II) complex was found to form 1:1 adducts with ZnCl_2 or ZnBr_2 . The two complexes are isomorphous. In the adduct structure the zinc atom is attached to the two oxygen atoms of the nickel compound leaving the remainder of the molecular geometry largely unchanged. Together with the two halogen atoms a tetrahedral environment $[\text{ZnO}_2\text{X}_2]$ is formed ($\text{X} = \text{Cl, Br}$), while the nickel atom retains its square planar $[\text{NiO}_2\text{P}_2]$ environment.

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