SYNTHESIS OF MOLECULAR PHOSPHONATES IN APROTIC SOLVENTS

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The transition metals complexes with the organophosphonate ligands of the general formula [RPO₃]²⁻ are much less studied compared to the carboxyl and similar compounds.¹ This is partly due to their coordination capabilities that allow the formation of multidentate insoluble complexes. Indeed, there are a large number of compounds with a multidimensional structure, such as coordination polymers (1D), layered structures (2D) and columnar or tubular (3D), however soluble molecular phosphonates (0D) are less known. The third group of periodic table is one of the less explored groups of elements. Although their well characterized phosphonic compounds have been prepared, they are not numerous.² Therefore, a series of experiments was conducted with selected phosphonic acids and their silvlated esters with anhydrous transition metal chlorides in an aprotic solvent environment such as THF and pyridine. The obtained products were studied by multinuclear NMR spectroscopy and in cases of successful crystal isolation by SCXRD. From the the reactions of tert-butyl phosphonic acid with yttrium(III) and lanthanum(III) it is $[\mu_3^{-t}BuP(O)_3]_4(YClpy_2)_2(YCl_2pyH)_2$ in pseudo-cubane geometry with $[Hpy]_3[YCl_6] \cdot 2py$ as a byproduct and $La_4[\mu_6$ bridged-square geometry.^{3,4} $^{t}BuP(O)_{3}_{2}[\mu_{4}-^{t}BuPO_{2}(OH)]_{2}(\mu_{2}-Cl)_{2}Cl_{8}(Hpy)_{6}$ with Reactions of other transition metals were studied as well. Reaction of anhydrous CuCl₂ with PhPO₃H₂ and KO^tBu in dry pyridine yieded two products. A product with formula $[Cu_6(\mu_3-PhPO_3)_4(\mu_4-PO_4)\cdot 12py]Cl$ with adamantane-like structure and $(Cupy)_6(\mu_3-PhPO_3)_4(\mu_4-PO_4)\cdot 12py]Cl$ with adamantane-like structure and $(Cupy)_6(\mu_3-PO_4)\cdot 12py]Cl$ with adamantane-like structure adamantane-like $PhPO_{3}_{4}(\mu_{4}-PhPO_{3})_{2}$ with cluster geometry. Reaction of salicylphosphonic acid $(salPO_3H_2)$ with CuCl₂ and KO^tBu in dry pyridine produced 1D product $[Cupy_4(salPOH_2)_2]_n$.

References

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