

Structural Systematics of Complexes of Lanthanoid Picrates with Unidentate O-donor Ligands

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Structures as determined by single crystal X-ray methods for lanthanoid(III) compounds for series of simple homoleptic species with diverse ligands frequently display variations entailing a diminution in coordination number (C.N.), a consequence of the variation in the size of the atoms/ions due to the lanthanoid contraction'. A change from C.N. nine to eight is common, clearly separating compounds of the light/early' or heavy/late' metal atoms. Earlier work on the complexes of the lanthanoid(III) picrates arose out of the exploration of simple reagents which might usefully exploit lanthanoid ion properties for purposes such as solvent extraction. They are also of potential synthetic utility because of their relatively high solubility in apolar solvents. Present work includes a systematic structural study of hydrated lanthanoid picrate complexes (including those of yttrium) with a selection of dipolar aprotic solvent ligands, namely trimethylphosphate (tmp'), dimethylsulfoxide (dmsO'), hexamethylphosphoramide (hmpa'), N,N'-dimethylacetamide (dma'), N-methylpyrrolidinone (nmp') and octamethylpyrophosphoramide (ompa'), all liquids at room temperature and all unidentate. This work aims not only to establish structural domains of existence' with a concomitant consideration of the associated stereochemistry for these related series of rare earth complexes, but, also, to enhance our understanding of metal ion solvation and the interactions of aromatic groups within these types of crystal structures.