

Title: Synthesis of metal complexes of TMT³⁻, TTPA³⁻ and 2-bromobenzoic acid and their characterization by X-Ray diffraction

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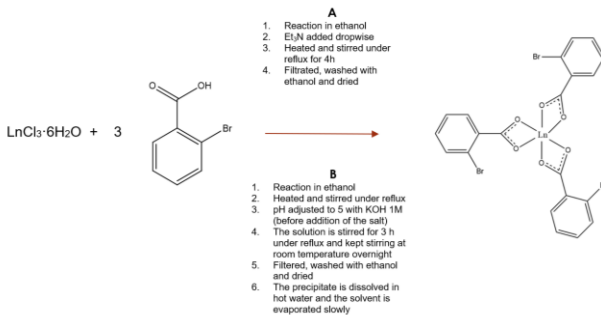
This research project includes several syntheses mainly based on the preparation of metal complexes using different types of ligands and their characterization by X-Ray diffraction.

Firstly, the synthesis of indium and tin complexes of 2,4,6-trimecapto-1,3,5-triazine acid were carried out using its deprotonated form (TMT³⁻). Its versatility of coordination with some metals is due to the presence of two kind of donor atoms (N and S) in its structure and this kind of complexes are widely studied and applied for heavy metal ions elimination in industrial wastewater.

3,3',3''-[1,3,5-triazine-2,4,6-triyltris(thio)]tris-acetate was synthesized to use it as a ligand to form 1,3,5-triazine-based compounds. Its ability of complexation with metal ions was proved by preparing Cu²⁺, Ni²⁺ and Co²⁺ complexes.

Finally, the preparation of the chlorides from the oxides of some lanthanoids (Dy³⁺, Gd³⁺ and Ho³⁺) was needed to prepare lanthanoid complexes of 2-bromobenzoic acid. Two different reactions were tried to get the best conditions to obtain a good yield and crystals. Then, the structures of the lanthanoid complexes were studied and characterized by X-Ray diffraction. These complexes have received much attentions because of having good fluorescence properties, high internal quantum efficiency and a good narrow strong emission band.

In the first synthesis, the product was not obtained successfully since the X-Ray diagram collected corresponds to one of the reactants (TMT³⁻). In the second one, the synthesis of the ligand (TTPA³⁻) was possible but it was not possible to isolate any metal complexes in the conditions of reaction. For that reason, the project is mainly focused in the last synthesis. So, in order to synthesize lanthanoid complexes two different reactions were carried out (Scheme 1).



Scheme 1 Synthesis of lanthanoid complexes of bromobenzoic acid following procedures A and B

Dysprosium, gadolinium and holmium complexes of 2-bromobenzoic acid were analysed in the X-Ray diffractometer. In these diagrams, the firsts peaks are in the same position and although the intensities are not the same, it means that lanthanoid complexes have the same unit cell. In other words, they are isomorphous.

In order to get information about their unit cell parameters and structure, all complexes were recrystallized in hot water until good crystals were obtained. Only in the case of Gd-complex was possible. So, Gd-complex was analyzed in the single crystal X-Ray diffractometer. The values obtained were not valid due to the mosaicity but knowing that lanthanoid complexes are isomorphous, it can be said that the lanthanoid complexes synthesized in this project have the same unit cell and structure as Nd-complex which unit cell parameters (Table 1) and structure (Figure 1) have already determined in previous studies.

Table 1 Unit cell parameters and Crystal System from Nd-complex

Parameters	Nd-complex
a (Å)	7.1041
b (Å)	12.8740
c (Å)	25.9505
α (°)	101.675
β (°)	91.588
γ (°)	90.481
System	Triclinic

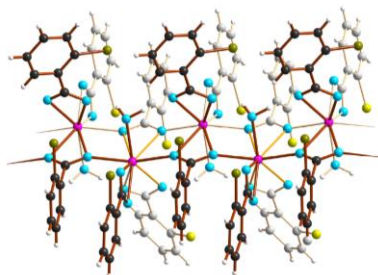


Figure 1 Structure of lanthanoid complexes of 2-bromobenzoic acid

The structure for lanthanoid complexes is the same with the difference that the distances of the bonds between the lanthanoid and the oxygen atom of the ligand decrease when the size of the lanthanoid is bigger due to lanthanoid contraction.