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HETEROMETALLIC LANTHANIDE(III)-BISMUTH(III) POLYAMINOPOLYCARBOXYLATE COMPLEXES: SYNTHESIS AND CRYSTAL STRUCTURE

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Modern coordination chemistry increasingly turns to metal compounds, special emphasis being recently paid to heterometallic complexes that exhibit a wider range of valuable properties when compared to homometallic compounds. The preparation of multimetallic complexes, most frequently, enables their nanoscopic dimensions to be combined with cumulative action of the component metals, and can lead eventually to novel or enhanced valuable characteristics.

Among the heterometallic compounds, bismuth based species have become of tremendous importance due to the great demand for advanced materials with applications in electronics, optics and catalysis. On the other hand, lanthanide-containing compounds possess interesting luminescence properties, which have found application in lighting, lasers, optical telecommunications, medical diagnostics and various other fields [1]. The combination of a lanthanide and bismuth within the same heterometallic complex offers opportunities to modify 4f-metals optical properties. It has been recently demonstrated that Bi(III) can be a sensitizer of lanthanide luminescence in the visible and near-infrared spectral region [2].

In this context we synthesized and investigated several series of heterobimetallic coordination compounds with different lanthanide(III) ions, Ln:Bi ratio, polyaminopolycarboxylate (PAPC) ligands and inorganic anions of general formula $Ln\{Bi(PAPC)\}_mX_{3-m}\cdot nH_2O$ and $Ln\{Bi(dtpa)\}NO_3\cdot 10H_2O$ (Ln(III) = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb; X = NO_3^-; ClO_4^-; NCS^-, CH_3COO^-; PAPC = $edta^{4-}$, $cdta^{4-}$, n = 5 - 11, m = 1 - 3). The polyaminopolycarboxylate ligands involved in the preparation of the complexes were ethylenediaminetetraacetate ($edta^{4-}$), cyclohexane-1,2-diaminetetraacetate ($cdta^{4-}$) and diethylenetriaminepentaacetate ($dtpa^{5-}$).

Single crystal X-ray diffraction study and IR spectroscopy results demonstrated that, depending on the lanthanide and inorganic anion nature, two series of isomorphous complexes are usually formed: Ce-Tb and Dy-Yb for $edta^{4-}$, $cdta^{4-}$ and NO_3^- species; Ce, Nd and Pr, Sm-Yb for $edta^{4-}$ and NCS^-; Ce-Eu and Gd-Yb for $cdta^{4-}$ and NCS^-. According to IR spectra, the compounds with $dtpa^{5-}$ and NO_3^- species generate only one isostructural series. In all the compounds, bismuth is the metallic specie that always coordinates the PAPC chelating agents while lanthanide(III) ions coordinate water molecules and carboxylic oxygen atoms of Bi-PAPC moieties. The crystal packing consolidation is performed by Ln aquated cationic moieties which coordinate by means of bridging carboxylic oxygen atoms to $Bi(edta)^-$ or $Bi(cdta)^-$ anionic aggregates, assembling them into 2D or 3D infinite networks, depending on the lanthanide, PAPC and inorganic anion. Most frequently the coordination number of Bi(III) ions is eight, though the values of nine and even ten (in $Ln\{Bi(edta)\}(NO_3)_2\cdot 7H_2O$, Ln = Ce-Eu) are also possible. The same characteristic for lanthanide(III) is nine or eight.

References

[1]. Martinus H.V. Werts, *Sci. Progress*, 2005, 88, 101 (and references therein).
[2]. Zeng X. et al. *J. Luminescence,* 2006, 121, 1.

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