

MS36-O2

Unexpected structural properties of Ln(III)-complexes formed with the heptadentate AAZTA ligand

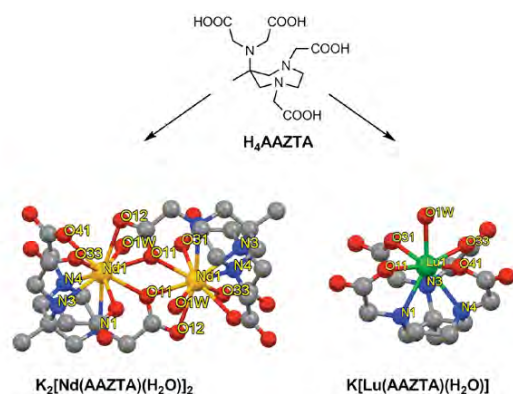
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The rich variety of magnetic, optical and radiochemical properties of lanthanide(III)-ions (Ln^{3+}) is the reason of the large number of applications of Ln(III)-complexes in several areas of chemistry, biology, medicine and materials science. *In vivo* applications requires very robust Ln(III)-complexes characterized by high thermodynamic and kinetic stability in order to limit the competition reactions with endogenous species. **AAZTA** (Scheme 1) is a mesocyclic chelating agent. Coordination properties of **AAZTA** towards a wide array of metal ions indicates its remarkable affinities for Ln(III)-ions.¹ Even if the Ln(III)-ions are very similar, detailed physico-chemical characterizations reveal that the thermodynamic and the kinetic properties, the exchange rate and mechanism of the inner sphere water molecule/s of $[\text{Ln}(\text{AAZTA})]^-$ complexes formed with smaller and larger Ln(III)-ions differ considerably.^{1,2} To explore the origin of the different physico-chemical properties of $[\text{Ln}(\text{AAZTA})]^-$ complexes, the structural properties of $[\text{Nd}(\text{AAZTA})]^-$, $[\text{Er}(\text{AAZTA})]^-$, $[\text{Lu}(\text{AAZTA})]^-$ and $[\text{Sc}(\text{AAZTA})]^-$ were determined by single crystal X-ray diffraction analysis. Crystals of $[\text{Ln}(\text{AAZTA})]^-$ complexes were obtained from a mixture of water and ethanol in the presence of guanidinium, K^+ and/or NH_4^+ counter ions. Crystals of $[\text{Nd}(\text{AAZTA})]^-$ (Scheme 1) are characterized by the presence of dimers. Three carboxylate groups behave as monodentate, while the fourth bridges the adjacent centrosymmetrically related Nd(III) ion, where one of the two oxygen atoms is shared between the two Nd(III)-ions. The coordination geometry in $[\text{Nd}(\text{AAZTA})(\text{H}_2\text{O})]^-$ is a distorted bicapped square antiprism with the capping positions occupied by a N atom and one O atom of the bridging carboxylates. One plane of the antiprism is formed by three carboxylate O and the water O atoms, and the other by two N and two carboxylate O atoms. In the $[\text{Lu}(\text{AAZTA})]^-$ complex, the Lu(III) ion is directly bound to seven donor atoms of the **AAZTA** ligand, octa-coordination being completed by the water O atom in the capping position. The coordination polyhedron of Lu(III) in $[\text{Lu}(\text{AAZTA})(\text{H}_2\text{O})]^-$ can be described by an irregular dodecahedron defined by a 1:4:3 stack of water O atom and of two nearly parallel planes formed by four carboxylate O and three N atoms. This coordination geometry (of idealized C_s symmetry) is unusual and it was not reported in the thorough stereochemical analysis proposed for ideal 8-vertex polyhedra, where 11 different cases were considered.³ By taking into account the structural properties of $[\text{Nd}(\text{AAZTA})(\text{H}_2\text{O})]^-$ and $[\text{Ln}(\text{AAZTA})(\text{H}_2\text{O})]^-$, the different physico-chemical properties might

be explained by the different coordination geometry of $[\text{Ln}(\text{AAZTA})]^-$ complexes formed by the smaller and larger Ln(III)-ions.



Scheme 1. Structures of H_4AAZTA ligand, $\text{K}_2[\text{Nd}(\text{AAZTA})(\text{H}_2\text{O})_2]$ and $\text{K}[\text{Lu}(\text{AAZTA})(\text{H}_2\text{O})]$ complexes

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MS36-O3

Mixed ligand Ni Werner complexes: enhanced selectivity and hydrogen bonding frameworks

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A mixed-ligand approach in the synthesis of Werner complexes with central nickel metal and thiocyanate anions with ligands of different aromatic or hydrogen bonding functionalities formed structural intricacy. In the selectivity of xylene isomers, differentiation showed that meta xylene was favoured over the other isomers, ortho xylene (ox), para xylene (px) and ethylbenzene (eb) in the co-ordination with the host $\text{Ni}(\text{NCS})_2(\text{isoquinoline})_2(4\text{-phenylpyridine})_2$.¹ The arrangement of the rigid isoquinoline² and the flexible 4-phenylpyridine ligands in trans positions gave the host flexibility to pack meta xylene more intimately than the other isomers. The outcome of the selectivity, $\text{mx} > \text{eb} > \text{ox} > \text{px}$, was confirmed by Hirshfeld surface analysis and void spacing determinations. The ‘tunability’ of the crystal structures arises from the transformation of the nature and size of the inclusion cavities.³ Attractive functionality using hydrogen bonding of the ligands was reflected in the structure of the complex, $\text{Ni}(\text{NCS})_2(\text{nicotinamide})_2(\text{isonicotinamide})_2$. Close packing in the crystal was realised. The complex arrangement of the host showed hydrogen bonding in different directions with amide bonding between the functional groups of the ligands and sulphur of the neighbouring host anion. The use of nickel as the metal centre gives the advantage of geometries not easily accessible in organic structures.

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