

SHORT COMMUNICATION

Synthesis and characterization of a novel (glycinato-N,O) yttrium(III) complex

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A novel yttrium(III) complex with glycine has been synthesized starting from tris(ethanedioato-O,O)yttrium(III) by the substitution of the acetylacetonato chelate ligands with glycine. The reaction product was purified by ion-exchange chromatography and characterized on the basis of infrared spectroscopy. The structure of the product was tentatively established as tris(glycinato-N,O)yttrium(III) dihydrate.

Keywords: yttrium(III) complexes; glycinato-N,O chelates, IR spectroscopy.

INTRODUCTION

Coordination chemistry of tris(aminocarboxylato-N,O) complexes of trivalent transition metals has continually been in focus for many decades.¹ A number of complexes of the general formula $M^{III}(aa)_3$ (where aa = bidentate aminocarboxylato-N,O chelate) have been prepared, characterized by a variety of physical methods, and studied using chemical, kinetic, thermodynamic, photochemical and computational techniques.²

However, it is still possible to find gaps in the chemistry of $M(aa)_3$ complexes across the periodic table of elements. A notable example is the scarcity of data on lanthanide complexes with aminocarboxylato-N,O bidentate chelate rings. In this work an attempt to prepare a complex of a tris(bidentate) type of yttrium(III) with glycine is described. Yttrium chelates have attracted much attention lately due to their potential application as tumour-targeting contrast agents in magnetic resonance imaging,^{3–5} and as luminescent bio-markers,⁶ let alone their significance in basic coordination⁷ and organometallic⁸ chemistry. From this study we expect to gain some further insight into the nature of metal–ligand interaction between coordinated carboxylato oxygen (as a supposedly anisotropic ligand⁹) and Y(III). It will eventually provide a basis for the parametrization of a molecular mechanics force field for amino(poly)carboxylate complexes of lanthanides, which is one of our long-term goals.

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EXPERIMENTAL

Tris(ethanedioato-O,O)yttrium(III) trihydrate was prepared according to the procedure of Sands et al.¹⁰

Tris(glycinato-N,O)yttrium(III) dihydrate. In 100 mL of ethanol (60 %) 6 g of tris(ethanedioato-O,O)yttrium(III) trihydrate was dissolved, and the solution was heated up to the boiling point in order to initiate the hydrolysis of the acetylacetonato complex. The solution was then cooled to ambient temperature and mixed with a previously prepared aqueous solution of glycine (4.6 g in 50 mL of water). The pH of the mixture was then adjusted to 5–6 and maintained at 30 °C under constant stirring for a period of 12 hours. After subsequent removal of the solvent under reduced pressure, a yellowish-white precipitate was obtained, which was filtered off, washed with abs. ethanol, and dried at ambient temperature. In this way 3.6 g of a water-soluble solid was obtained. The solid was dissolved in a minimal amount of water and passed in turn through cationic and anionic Dowex ion-exchange columns eluted with water. The resultant solution was concentrated in a vacuum-evaporator and left overnight to crystallize. Anal.: Found: C, 20.63 %, H, 4.7 %, N, 12.55 %; calculated for $Y(\text{Gly})_3 \cdot 2\text{H}_2\text{O}$: C, 20.7 %, H, 5.43 %, N, 12.10 %.

Infrared spectra of reactants and the reaction product were measured on a Perkin-Elmer FTIR 172 instrument using the KBr pellet technique.

RESULTS AND DISCUSSION

The experimental procedure was conducted in an attempt to substitute acetylacetonato with glycinato ligands. Namely, the tris(ethanedioato-O,O) complexes of yttrium(III) as well as of other trivalent lanthanides are known to undergo facile hydrolysis in aqueous media yielding mixed hydroxo and ethanedioato species.¹¹ In the presence of excess glycine these hydrolysis products are expected to form chelate (glycinato-N,O) species. At pH 5–6 glycine is present predominantly in the zwitterionic form. Therefore, it can be easily coordinated to Y(III) *via* the carboxylate oxygen causing the ammonium to deprotonate (by elimination of H₂O molecule from Y(III)-hydroxo species). The latter step is favoured by the chelate effect of glycine.

A strong support for the proposed overall course of the substitution reactions stems from the fact that the same product was obtained using a range of different mole ratios of tris(ethanedioato-O,O)yttrium(III) to glycine. Even with glycine as the limiting reagent the identical product was obtained after removal of unreacted tris(ethanedioato O,O)yttrium(III).

The solid-state infrared spectrum of the glycinato complex of yttrium(III) in the region 2000–400 cm⁻¹ is presented in Table I together with the assigned spectrum of crystalline glycine.¹² The differences in the positions of the infrared absorption maxima between the free glycine (zwitterion) and its yttrium(III) complex are small but consistent with our proposed structure of the complex having bidentately coordinated (glycinato-N,O) ligands. The characteristic features pertain to the vibrations associated with the COO group. They are indicated in bold in Table I. Thus, $\nu_a(\text{COO})$ is shifted to a higher frequency (from 1616 to 1636 cm⁻¹) and the $\nu_s(\text{COO})$ to a lower frequency (from 1413 to 1400 cm⁻¹); both wagging and rocking COO vibrations are shifted to higher frequencies (Table I) indicating a metal–oxygen coordination.¹³

Since our synthesis and ion-exchange chromatography yielded only one pure substance, we were not able at this stage to identify the geometrical configuration of the

product in terms of *fac* and *mer* isomerism characteristic for $M(\text{Gly-N,O})_3$ species. In addition, our results do not exclude a possibility of the augmentation of the coordination sphere¹⁴ with one of the H_2O molecules assumed to be lattice water. However, in either case it is highly unlikely that the glycinato ligands are not bidentately coordinated. Further structural investigations along these lines are in progress.

TABLE I. The observed infrared frequencies (cm^{-1}) for the crystalline glycine, and glycinato Y(III) complex, with tentative assignments

Glycine	Y(Gly) ₃	Assignment
1630		shoulder
1616	1632	COO ⁻ asym. stretching
1507	1500	
1468	-	
1445	1440	CH ₂ bending
1413	1400	COO ⁻ sym. stretching
1333	1332	CH ₂ wagging
-	1300	
1132		NH ₃ ⁺ rocking
	1123	NH ₂ rocking
1111		NH ₃ ⁺ rocking
	1100	NH ₂ rocking
1033	1040	CN stretching
911	927	CH ₂ rocking
893	893	CC stretching
699	700	COO ⁻ bending
609	620	COO ⁻ wagging
502	520	COO ⁻ rocking
435		
419	421	

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НОВОГ (ГЛИЦИНАТО-N,O) ИТРИЈУМ(III) КОМПЛЕКСА

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Супституцијом координаног ацетилацетоната глицином у трис-бидентатно координаном итријум(III) комплексу добијен је нов глицински комплекс итријума(III),

koji je после пречишћавања јоноизмењивачком хроматографијом окарактерисан на основу инфрацрвених спектра. На основу карактеристичних померања инфрацрвених трака за карбоксилатни фрагмент предложена је трис(глицинато-N,O) структура за ову супстанцу.

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