



Review

Carboxylates of rare earth elements



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ABSTRACT

Rare earth carboxylates constitute an enormous group of compounds with various structures and properties. The carboxylate group may be bonded to the metal cations in several ways. The structural aspects of the coordination modes are presented and discussed from the statistical point of view and the most typical groups of carboxylate complexes are reviewed. Data concerning the thermodynamics of formation of the lanthanide, mostly Eu(III), complexes, have been aggregated and briefly analyzed. The electronic spectroscopy of lanthanide carboxylates, mostly focused on analysis of hypersensitive transitions, is discussed for simple carboxylates, acyclic aminopolycarboxylates and dipicolinates, as exemplary systems.

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1. Introduction

Carboxylic acids form an enormous class of compounds with diverse structures and properties. As ligands they offer almost unlimited possibilities to design metal complexes with customized properties. This and two other facts, namely, that: (a) rare earth (+3) ions (RE^{3+}) readily form complexes with carboxylate ligands and (b) the synthesis of relevant complexes may be often performed at undemanding conditions, usually in water solutions, ascertain the role of carboxylates in rare earth chemistry. Application of hydrothermal methods has led to synthesis of many polymeric and cluster compounds, often with very sophisticated structures. Extensive investigations have resulted, for instance, in more than 10000 crystal structures of Y and Ln carboxylates deposited in the Cambridge Structural Database (CSD) [1]. Motivations to study this class of compounds are various and usually depend on the selected metal, as most of these elements, although similar from the chemical point of view, possess diverse spectroscopic and magnetic properties. The elements that are spectroscopically and magnetically silent (Y, La, Lu) have been used to construct metal-organic frameworks, as well as to provide neutral matrices for active rare earth dopants. It may be interesting to find how the carboxylates are distributed along the rare earth series. In CSD there are 401 structures of Y carboxylates, 920 of La, Ce - 541, Pr - 671, Nd - 950, Pm - 0, Sm - 814, Eu - 1365, Gd - 1209, Tb - 1103, Dy - 974, Ho - 391, Er - 653, Tm - 135, Yb - 403 and Lu - 117. One may easily notice a rather distinct preference for luminescent Eu and Tb compounds, as well as for magnetic Gd^{3+} cation. In this review the magnetic properties will not be discussed, as these aspects of Ln carboxylates chemistry have been fragmentarily discussed in a few reviews [e.g. [2–5]] and extensive presentation of these aspects lies outside of the scope of the present paper. Likewise, complexes of lanthanides with aminoacids have been reviewed in [6] and the reader is referred to this publication. It will be tacitly assumed that the rare earth elements, which in the present work are limited to Y, La and lanthanides, i.e. without Sc, are in the trivalent state; other cases will be explicitly indicated. Also typical oxidation states of other elements, like Cu(II), Zn(II) etc. will not be specified. The reader must be warned that in some formulas molecules of solvation, which were deemed unessential for the discussion, such as e.g. uncoordinated water, have been omitted. All the statistics and examples presented below are based on CSD, 2016 release. Apart from that general features of stability constants and thermodynamic data of complexation reactions of lanthanide with selected carboxylates in aqueous solution will be discussed and selected spectroscopic questions will be reviewed.

2. List of abbreviations

dmf *N,N*-dimethylformamide;
 H₄cdta 1,2-cyclohexanediaminetetraacetic acid;

H₃cit citric acid;
 H₄dota 1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid;
 H₅dtpa diethylenetriaminepentacetic acid;
 H₄edta ethylenediaminetetraacetic acid;
 H₄egta ethylene glycol-bis(2-aminoethylether)-*N,N,N',N'*-tetraacetic acid;
 H₂fum fumaric acid;
 H₃nta nitrilotriacetic acid;
 H₄obeta 2,2'-oxybis(ethylamine)-*N,N,N',N'*-tetraacetic acid;
 H₂oda oxydiacetic acid;
 H₂ox oxalic acid;
 H₄pdta propylenediaminetetraacetic acid;
 H₂phth phthalic acid;
 Hpiv pivalic (dimethylpropanoic) acid;
 H₄pmdc 4,6-pyrimidinedicarboxylic acid;
 H-*m*-pyc *m*-pyridinecarboxylic acid (*m* – locant);
 H-*m*-pyc-*N*-O *m*-pyridinecarboxylic acid *N*-oxide;
 H₂-*m,n*-pydc *m,n*-pyridinedicarboxylic acid;
 H₄pyfc 2,3,5,6-pyridinetetracarboxylic acid;
 H₃-2,4,6-pytc 2,4,6-pyridinetricarboxylic acid;
 H₂-*m,n*-pzdc *m,n*-pyrazinedicarboxylic acid;
 H₂tart tartaric acid;
 H₆ttha tetraaminetriethylenhexacarboxylic acid;
 H₂seb sebamic acid;
 phen 1,10-phenanthroline;
 RE a rare earth element (Y or Ln);
 ⌊A-B...C⌋ ring starting from A, going through B, ..., to C and returning to A.

3. Coordination modes of carboxylate group

The carboxylate group has two donor atoms, which in turn may be coordinated to one or two (and on rare occasions to three) metal cations. This gives rise to the coordination modes which are presented in Fig. 1, along with the numbers of crystal structures in which the relevant mode occurs.

It should be observed that the nomenclature of the coordination modes is not entirely fixed. At this point we would like to point to a convenient way devised by S.G. Harris [7]. The coordination pattern is namely described (for the case of the carboxylate groups) by the symbol $X.Y_1Y_2$, where X is the total number of the coordinated metal cations and Y_i is the number of metal cations coordinated to i -th donor. The Harris symbols for each mode are given in the caption of Fig. 1. The modes shown in this Figure concern only the systems where the rare earth cations are the only metals involved in bonds with the carboxylate group. There are many structures in which the $-COO^-$ group is linked both to a RE^{3+} cation and to a metal cation of the 1 or 2 group, or to a d -block element.

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