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Review

Sensing and activation of anionic species by polyamine-based metal complexes

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ABSTRACT

The role of metal complexes with polyamine ligands in selective binding of anions and their possible use as optical chemosensors or biologically relevant hydrolytic agents for anionic substrates will be discussed on the basis of some study cases from the work of the authors, with particular emphasis on the cooperative action of metal cation and polyamine receptor in both the processes of interaction and sensing/activation.

Andrea Bencini received his Ph.D. in Chemistry from the University of Firenze, Italy, in 1993. In the same year he was appointed tenure researcher and in 2003 associate professor of General and Inorganic Chemistry at the Faculty of Science of the University of Firenze. The research activity of Andrea Bencini is located at the interface between supramolecular and coordination chemistry and includes the design and synthesis of optical chemosensors for metal cations and anions of biological or environmental interest and development metal complexes to bind and/or react with small molecules or anions, such as CO_2, NO, superoxide, and other reactive oxygen species. He is author of more than 200 publications in peer-reviewed journals.

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Vito Lippolis graduated in chemistry in 1991 at the University of Pisa, Italy, and in the same year gained a diploma in chemistry at the "Scuola Normale Superiore" of Pisa. In 2000 he received his Ph.D. degree from the University of Nottingham, UK, under the supervision of Professor Martin Schröder. In 2001 was appointed to the chair of inorganic chemistry at the University of Cagliari, Italy. He has published about 250 publications and his research interests at the moment mainly include: Supramolecular chemistry and crystal engineering, coordination chemistry of macrocyclic ligands and development of molecular sensors and ionophores for heavy metal ions and anions, study of the interaction between chalcogen donor molecules and halogens and inter-halogens, synthesis and study of new metal-dithiolenes complexes for applications in the fields of laser technology and semiconductors.

Barbara Valtancoli received her Ph.D. in Chemistry in 1994 at the University of Florence. After a postdoctoral fellowship from 1994 to 1998 in 1999 she was appointed tenure researcher and in 2005 associate professor of General and Inorganic Chemistry at the Faculty of Sciences of the University of Florence. Barbara Valtancoli is the author of more then 170 scientific publications on international journals. Her research interests are mainly synthesis of polyamine ligands, thermodynamic study of complex formation and analysis of the binding ability of the complexes for anionic species. In the last few year, her research activity has been focused on fluorescent metal complexes capable to selectively recognize and sense anions as well as on transition metal complexes able to scavenge the superoxide anion, reducing its concentration both in vitro and in vivo.

Contents

1. Introduction

The design and synthesis of artificial receptors able to either recognize or sense selectively anionic species [1–7], or to act as enzymatic mimics in the activation of anionic species for bio-catalytic processes [8–12] has become a prominent and active field of research within the realm of "Supramolecular Chemistry" in the relatively young area of anion coordination chemistry.

When compared to metal ions, anionic species show larger sizes, variety of shapes, higher hydration energies within a wide scale of hydrophobicity and in some cases a limited pH range of existence due to a propensity to undergo protonation processes in water-containing solutions.

To tackle these specifics concerning the selective coordination and binding of both organic and inorganic anions, there are different synthetic strategies of artificial receptors at the molecular level, based either on non-covalent weak intermolecular interactions (H-bonding, π-stacking interactions, electrostatic interactions and hydrophobic effects) *via* topological complementarity, or on coordination-based metal–ligand covalent interactions. Following the latter strategy, the role of the metal centre(s) can be that of either to directly bind the anionic guest *via* the formation of a strong covalent bond, or to induce a geometrical pre-organization of the complex species, which determines host-guest complementarity of the binding sites for a better and efficient fit of the shape and size coordination requirements of anionic species.

In this short review, some examples from the work of the authors will be discussed about the use of metal complexes of polyamine ligands as receptors for performing sensing and enzymatic functions based on the selective recognition of targeted anionic species.

2. Sensing of anionic species by polyamine-based metal complexes

Anion recognition and sensing has recently received considerable attention because of the central role played by anions in biological, industrial and environmental processes. There is a great demand for extremely sensitive and selective analytical tools for the detection and monitoring of anions, especially toxic ones, in biological, environmental and industrial waste effluent samples. Applications can span from process control, to environmental monitoring, food analysis and medical diagnosis, to give some examples.