PHYSICO - CHEMICAL STUDIES ON SOME CERIUM COMPLEXES AND THEIR POSSIBLE APPLICATION FOR DECONTAMINATION PURPOSES

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NOTE

Besides to the work carried out in this thesis the candidate has post-graduated courses for two years in:

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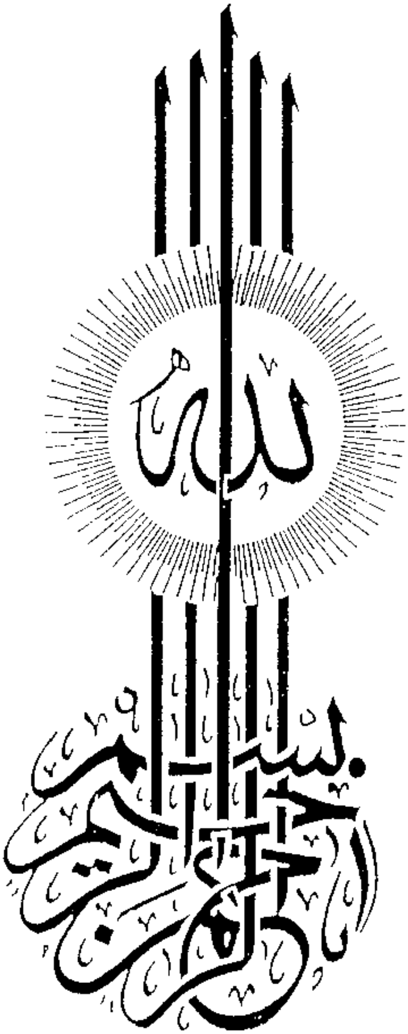

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OBJECT OF THE WORK

For the present, and in all probability also in the future, therapy for radioactive contamination require the lowering of radiation exposure, by an increase of radioelement extraction from the body by using chelating agents.

The polyaminopolycarboxylic acids, in particular, were used as decontaminating agents due to their superiority to all other chelating agents This is based upon their high affinity for a large number of metal ions, their water solubility and intermetabolic behaviour. On the other hand, increase in the number of amine and carboxylic groups in the chain of this organic family increases the value of the stability constant of the formed complex, therefore increase its power as decontaminating agent.

The aim of this work is to study (IN VITRO) the chelation of ionic tri- and tetravalent cerium with tetraethylenepentaaminehepta acetic acid [TPHA], to investigate the composition and the stability constant of the formed complex, and to illustrate the reducing power of [TPHA]. Further more, the chelation of hydrolysis states of tri- and tetravalent cerium by [TPHA] was investigated.

CHAPTER I

INTRODUCTION

Chapter (1)

INTRODUCTION

[illegible] METAL CHELATE COMPOUNDS:

(1) Definition of Terms:

When a metal ion combines with an electron donor, the resulting substance is said to be a complex, or co-ordination compound. If the substance which combines with the metal contains two or more donor groups so that one or more rings are formed, the resulting structure is said to be a "chelate compound", or metal chelate, and the donor is said to be a "chelating agent". The electron-pair bonds formed between the electron-accepting metal and the electron-donating complexing or chelating agent may be "essentially ionic" or "essentially covalent" depending on the metals and donor atoms involved.

Complexes and chelates are formed by nearly all the metals of the periodic system. Although the number of known chelating and complexing agents is very large, the donor atoms which undergo combination with the metal are restricted to the strongly non-metallic elements of Groups V and VI. In recent years a number of new aminopolycarboxylic acids which have the special property of forming water-soluble chelates have come into wide spread use.

(2) WERNER's(1) Co-ordination Theory:

In 1891, **WERNER** proposed his co-ordination theory to account for the phenomenon by which apparently stable, saturated molecules combine to give so-called "molecular complexes". Metals were found to form compounds, often by the addition of quite stable molecules which the metal displayed valency, which greater than its oxidation valency. For example, when ammonia is added to a solution of copper sulphate, the colour of the solution turns from a pale to an intense blue. If by evaporation and crystallisation an attempt to separate the copper sulphate from the water, it could obtain not $CuSO_4$ but $Cu(NH_3)_4SO_4$

This hypothesis was built essentially around the assumption that certain atoms may combine with a definite maximum number of other atoms, molecules, or radicals. This number called the co-ordination number, was usually six, sometime four, and infrequently two or even eight, depending on the central atom involved mainly.

The complex was considered as composed of a central positive ion which attracted ligands to itself by electrostatic forces. If the ligands were themselves negative ions, the attraction was simply the attraction of the opposite charges.

If the ligands were such neutral molecules as water or ammonia, the attraction was ascribed to the dipole moment of such molecules. "It is sometimes forgotten that quantum mechanics has not introducted any type of forces. In the most sophisticated of the quantum mechanical treatments of such complexes, the forces of attraction responsible for complex formation are still electrostatic in nature".

(3) Electronic Theory of Valence and Complex Formation:

WERNER's co-ordination theory displaced the structural theory for inorganic substances by explaining many properties of compounds through the concept of complex formation. On the other hand, the theory emphasized a false distinction between the structures of organic and inorganic compounds, and it had an inherent weakness in that it postulated two different kinds of valence for inorganic substances (primary and secondary valence bonds) without any theoretical justification for their existence. The apparent conflict has now been resolved by the development of the electronic theory of valence which not only reconciled covalence and electrovalence but introduced a third type of bond (the co-ordinate covalent bond) in which both electrons are supplied by the same atom.

It is noteworthy that the formation of co-ordination complexes falls under the electronic theory of acids and bases proposed by LEWIS. The neutralisation of an acid with a base, according to the LEWIS concept, always involves the combination of an acid (electron acceptor) with a base (electron donor) with the formation of a co-ordinate bond.

The tendency for complex formation with donor molecules may be interpreted as the tendency for metal ions to fill up unoccupied orbitals and thereby approach the electronic configuration of an inert gas.

The cyclic compounds, in which a metal is jointed to two or more donor groups of a single molecule or ion, are particularly important since they have exceptionally high stability and, in many cases, have remarkable and valuable properties. Such structures are complexes in the WERNER sense since they have co-ordinate bonds. This type of ring formation was named (chelation) by MORGAN and DREW and the term has been used to cover all types of ring systems with metals and with hydrogen, without regard to the nature of the chemical bond involved, also the terms unidentate, bidentate, tridentate, quadridentate etc., were proposed by MORGAN to denote complexes formed with molecules or ions containing one, two, three, four, etc., donor groups respectively. Obviously, complexes with unidentate substances would not involve chelation.

(4) Stability Constant of Chelate:

In the consideration of matters relating to chelation, it must have some quantitative measure on which to judge the various materials. This is known as the stability constant, which is the logarithm of the formation constant, or if preferred of the reciprocal of the dissociation constant of a reversible reaction. The chelate stability constant is generally taken as the equilibrium constant for the reaction (2), in which metal chelate is formed the hydrated metal and the most basic (most highly dissociated) form of the chelating agent.

$$M^{+N} + X^{-A} \rightleftharpoons MX^{N-A}$$

$$M_{MX} = \frac{[MX^{N-A}]}{[M^{+N}][X^{-A}]}$$

where M^{+N} is the metal ion, X^{-A} is the ligand, [ ] indicate the molar concentration, and K_{MX} is the constant applies to a specific temperature.

Since the activation of ions in solution is strongly influenced by the total ionic concentration of the solution, it is necessary to maintain a constant electrolyte concentration, if the equilibrium constant given above is to be a true constant. Consequently, measurements of chelate formation constants are usually carried out at controlled concentration of an added inert electrolyte. It is seen, therefore, that these so-called "concentration constants", which are obtained from stoichiometric measurements of the above equilibrium, may be strictly applied only at the specified temperature and electrolyte concentration.

(5) Chelation of Rare Earth Elements with Polyaminopolycarboxylice Acids:

On the basis of many well established instances of ionic bonding in rare earth metal compounds, it has been quite generally concluded that the stabilities of complexes derived from the tri-positive cations of these metals should increase with decreasing cation radius or increasing atomic number. An examination of stability constant data for a number of complexing agents(3) reveals that in all instances there is a larger discontinuity at gadolinium than the corresponding discontinuity in radii(4), would suggest and that with some