

PHYSICO-CHEMICAL STUDIES OF TERNARY COMPLEXES

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Abstract

The introduction of the nitrogen and sulphur atoms into the structure of organic compounds has often important consequences in their behavior toward metal ions. From the comparatively large atomic radius of sulphur atom and its electro negativity than nitrogen, one expects that sulphur containing ligand will form less stable complexes than those containing nitrogen but it has been observed that the affinity of sulphur for metal ions is often very close to the ligands containing nitrogen.

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Introduction

4f-metals including lanthanum and the succeeding fourteen lanthanide elements form the longest continuous series of chemically similar elements in the periodic table. The 4f transition series owes its existence to decrease in both potential energy and the spatial extension of 4f-orbitals immediately after lanthanum which allow preferential occupancy of these orbital's by differentiating electrons. Thus, e.g. the binding energy of a single 4f-electron drops from -0.95 eV for the lanthanum atom to -5.0eV for the neodymium atom. Although the 4f-orbitals are well outside the xenon structure and are thus unoccupied in the lanthanum atom, they are occupied in the neodymium atom. The ground state electronic configurations of the neutral lanthanide atoms do not show any absolute regularity in the occupancy of orbital's. However complete regularity is achieved among the highly charged Ln (III) species. There is also a discernible tendency, wherever possible to achieve the 4f and 4f configuration sooner than a strict nuclear charge sequence would dictate.

The filling of the 4f-shell in the lanthanides is accompanied by a sequential contraction in the sizes of the atoms and the ions. This contraction popularly referred to as the lanthanide contraction is more spectacular than the corresponding contraction which occurs as a "d"-shell is filled. The lanthanide contraction is a consequence of the imperfect shielding of one 4f-electron by another. As the nuclear charge (and thus the 4f-electron population) increases, the imperfect shielding due to the directed nature of the 4f-orbitals causes each 4f-electron to experience added electrostatic attraction by the nucleus. The lanthanide series has a 22% change in the ionic radii. 1.061Å for La (III) to 0.848Å for Ln (III). One of the consequences of the lanthanide contraction is the inclusion of Y (III) in the lanthanide series. The ionic radius of Y (III) (0.9Å) is intermediate between Ho (III) and Er (III) and its chemical behavior is normally identical with that of lanthanide ions.

However, the contraction does proceed sufficiently far to include scandium (= 0.731%).

The co-ordination numbers exhibited by the 4f-metal ions are generally varies from six to ten, bidentate ligands with smaller "bite" often yield complexes with higher co-ordination numbers. There are a few exceptions to this general observations; e.g., Bradley et.al. have prepared compounds of the general formula $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$; where the co-ordination number has been shown to be three for all the lanthanides. It may be mentioned here that the first case of an unusual eleven co-ordinate environment around lanthanide ion has been established by X-ray crystal structure

determination of penta aquo tris(nitrato) lanthanum (III) monohydrate. The stoichiometry of a lanthanide complex is also affected by the anions present in the complex. Anions such as nitrate, chloride, bromide, thiocyanate and sulphate compete with the ligand for co-ordination sites on the metal ion. Other anions such as perchlorate, tetraphenylborate and hexafluorophosphate do not generally co-ordinate to the metal ion and complexes with a maximum number of ligands are obtained when these are used as counter anions.

The introduction of the nitrogen and sulphur atoms into the structure of organic compounds has often important consequences in their behavior toward metal ions. From the comparatively large atomic radius of sulphur atom and its electro negativity than nitrogen, one expects that sulphur containing ligand will form less stable complexes than those containing nitrogen but it has been observed that the affinity of sulphur for metal ions is often very close to the ligands containing nitrogen as donor atom. Many investigations have been undertaken of the interaction of transition and inner-transition metal ions with nitrogen and sulphur containing ligands although in many cases the stereochemistry and electronic structures are reasonably well understood yet the structure and bonding in several metal complexes involving ligands nitrogen and sulphur donors have not been satisfactorily worked out.

Of the sulphur donor ligands thiosemicarbazones have perhaps not reviewed as much attention as dithiophosphate, dithiocarbamate, dithiolates, dithio- β -di-Ketonates, dithiooxamides or xanthates. A number of thiosemicarbazone ligands have been derived by simply condensing aliphatic, aromatic or heterocyclic aldehydes or Ketones with thiosemicarbazide compounds possessed wide spectrum of medicinal properties, including activity against influenza, protozoa, smallpox, certain kinds of tumour, tuberculosis, leprosy, bacterial and viral infections, psoriasis, rheumatism,

tripanosomiasis, coccidiosis, malaria and have been suggested as possible pesticides and fungicides.

It is interesting to note that in the formation of mixed ligand species, the trivalent lanthanides have a tendency to attain high co-ordination number forming more stable complexes. In recently years a number of review articles have appeared detailing lanthanide (III) complexes of Schiff bases. From our laboratory Agarwal et. al. and others have reported a number of lanthanide (III) complexes of various Schiff bases including hydrazones, semicarbazones and thiosemicarbazones.

A critical survey of the literature revealed that the mixed ligand complexes of La (III), Pr (III), Nd (III) and Sm (III) with hydroxybenzene-2-carboxaldehyde-2-furanthiocarboxyhydrazone (L_1H), pyridine-2-carboxaldehyde-1-thionaphthoylhydrazone (L_2H) as primary ligands and 2-carboxy-phenylazo-2-naphthylamine (L_1H) and 2-hydroxy-5-methyl-2'-carboxyazo-benzene ($L_2'H$) as secondary ligands have not been studied so far. In the present chapter, we report the syntheses of these complexes. The complexes have been characterized on the basis of analytical, magnetic, conductance and spectral (IR and reflectance) data.

REFERENCES

1. Singh, Nepal, Agarwal, Poonam and Gupta, Vinita, J. Indian Chem. Soc., 1984, 61, 94.
2. Agarwal, S.K., Kumar, Rajesh, Pokhariyal, G.P. and Tyagi, D.K., Asian J. Chem., 1991, Vol 3, No(4), 467.
3. (Mrs.) Shukla, P.R., (Miss) Minakshi, Pathak, K Ashish and Narain, Gopal, Indian Chem. Soc., 1990, 67, 678.
4. (Mrs) Shukla, P.R., (Miss) Bhatt, M. and Sharma, Mukesh Chandra, J. Indian Chem. Soc., 1989, 66, 192.
5. (Mrs.) Sharda, L. Nalancla, Ganorkar, and Rao, N. Rama, J. Indian Chem. Soc., 1995, 72, 439.
6. Shetti, S.N., Murty, A.S.R. and Tembe, G.L., J. Indian Chem. Soc., 1996, 73, 91.