

Synthesis and Characterization of Sc(III)-N- α -Naphthyl-Oxamic Acid Complex

VINOD KUMAR SHARMA

Department of Chemistry

College of Science, MLS University, Udaipur-313 001, India

The N- α -naphthyl oxamic acid is well known monobasic bidentate O-O-donor ligand. The scandium complex of N- α -naphthyl oxamic acid has been prepared for estimation of scandium metal. The complex is insoluble in organic solvent but soluble in hot mineral acids and strong alkali. The complex formed is thermally stable up to 250°C and has been characterised by elemental analysis.

INTRODUCTION

Oxamic acids¹⁻⁷ and their derivatives are known to play an important role as a ligand by virtue of their bonding coordination to metal ions. Earlier N- α -naphthyl oxamic acid (N- α -NOXA) was used to form metal complex with some of the lanthanides for their estimation. The ligand N- α -naphthyl oxamic acid behaves as a bidentate ligand and coordinates through the two oxygen atoms. In this communication synthesis of scandium(III) complex with N- α -naphthyl oxamic acid is being reported for estimation of scandium(III) ion. The metal complex formed is characterised by thermal and spectral analysis.

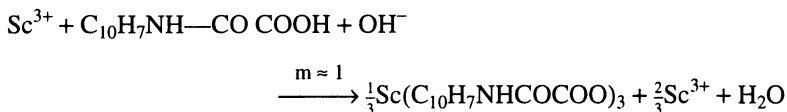
EXPERIMENTAL

All the chemicals used were of AR grade. Solutions were prepared in double distilled water. The metal solution was prepared by dissolving metal oxide in nitric acid followed by standardisation of metal oxalates with KMnO_4 .⁸ The ligand N- α -naphthyl oxamic acid was synthesised and purified by the reported method.⁹ The IR spectra was recorded with KBr pellets using Perkin-Elmer 783 spectrophotometer. The thermal analysis of the complex was recorded on a Stanton (mass flow) type automatic recording thermogravimetric balance at a heating rate of 5°C per minute. The pH titration was carried out using Philips pH meter, calibrated with 0.1 M potassium hydrogen phthalate solution for pH 4. The following system of pH titration was carried out keeping the total volume 50 mL and the ionic strength ($\mu = 0.1 \text{ M KNO}_3$) constant against 0.1 M KOH at room temperature.

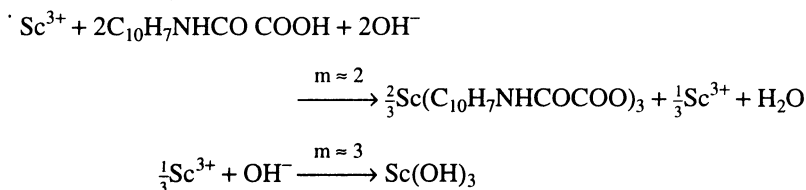
- 10 mL of 0.01 M Sc(III) nitrate solution.
- 10 mL of 0.01 M N- α -naphthyl oxamic acid [N- α HOXA]
- 10 mL of 0.01 M Sc(III) nitrate + 10 mL of 0.01 M [N- α NOXA]
- 10 mL of 0.01 M Sc(III) nitrate + 20 mL of (0.01 M) [N- α NOXA]
- 10 mL of 0.01 M Sc(III) nitrate + 30 mL of (0.01 M) [N- α NOXA]

RESULTS AND DISCUSSION

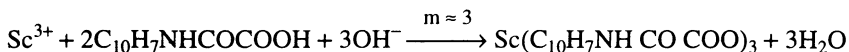
In the first set of potentiometric titration of scandium metal (a) a single sharp inflection at $m \approx 3$ with a pH = 9 to 10 shows the formation of metal hydroxide. In the second set of titration (b) shows a single sharp inflection at $m \approx 1$ which can be ascribed to the neutralization of carboxylic proton of the acid. The absence of second inflection however indicates the firm attachment of the proton of the imino-group even at pH = 11. In the third set of titration (c) Sc metal and 10 mL of ligand shows 1 : 1 system of metal ligand. The lowering in initial pH from 4.5 to 4 and appearance of a white precipitate from the beginning of the titration indicates the formation of 1/3 neutral species as per the following equation.



The formation of above neutral species is further supported by the presence of another inflection at $m \approx 3$ probably due to hydroxide in higher pH region (pH 10). In the set (e) when the metal ligand system is 1 : 2, the lowering in the initial pH with the appearance of the solid phase and two inflections at $m \approx 2$ and $m \approx 3$ probably corresponding to the following reaction:



In the set (e) 1 : 3 Sc(III) and N- α -naphthyl oxamic acid, a sharp inflection on $m \approx 3$ and formation of a white solid indicates the 1 : 3 neutral species.



Preparative studies

The potentiometric evidences for the formation of 1 : 3 Sc(III) N- α -naphthyl oxamic acid complex was confirmed by the preparative studies. In a 30 mL of (0.025 M) scandium nitrate solution taken in a beaker about 100 mL of (0.025 M) N- α -naphthyl oxamic acid was added with constant stirring. The white precipitate formed was filtered through a sintered crucible. The precipitate was first washed with hot water followed by cold water and finally with 10% alcohol. The precipitate was dried at 100–110°C in an air oven to a constant weight. The white precipitate is insoluble in water, benzene, chloroform, carbon tetrachloride but soluble in hot mineral acids and alkali. Microanalytical methods were used for elemental analysis. The metal content was estimated using appropriate method of analysis.¹⁰ The data are given in Table-1.

TABLE-1
PHYSICO-CHEMICAL DATA OF THE COMPLEX

Composition: $\text{Sc}(\text{C}_{10}\text{H}_7\text{NHCOCOO})_3$ Appearance: white crystalline (m.p. $203 \pm 1^\circ\text{C}$)

	Carbon	Hydrogen	Nitrogen	Scandium
Calculated	62.88	3.49	6.11	6.55
Found	62.80	3.54	6.18	6.60

Thermogravimetric study: The thermolysis of Sc(III) N- α -naphthyl oxamic acid has a horizontal portion up to 240°C indicating that the complex is stable up to 240°C . There is no loss of water up to this temperature. This shows that the complex has no loss of water of crystallisation. The complex decomposed rapidly up to 366°C . On plotting differential curve a characteristic peak is observed, which shows that the maximum decomposition of the complex is at 370°C . After 386°C there is a gradual loss in weight up to 600°C . In this stage there is a minimum loss in weight. Finally the metal oxide is formed at the temperature 600°C .

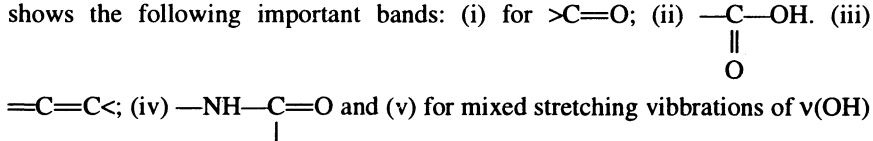
Gravimetric study: The alcoholic solution of the oxamic acid was added slowly with constant stirring to hot solution of scandium(III) nitrate, till the precipitation was completed. After cooling the precipitate at room temperature, it was filtered, washed and dried at 120°C . The N- α -naphthyl oxamic acid forms voluminous easily filterable chelates with a number of metal ions. However, the Li(I), Na(I), Mg(II), K(I), As(II), Sb(II), Bi(II) do not interfere in the quantitative analysis. Cu(II), Cd(II), Fe(III) and Co(II) ions can be masked with cyanide or thiocyanide or thiosulphate ions. Zr(IV) and Ti(IV) can be masked with hydrogen peroxide solution. Hg(II) can be masked by Γ ion by addition of excess of potassium iodide. The results of the gravimetric estimation are given in Table-2.

TABLE-2
GRAVIMETRIC ESTIMATIONS

Vol. of 0.025 M $\text{Sc}(\text{NO}_3)_3$ in mL	Weight of complex in mg		% error
	Practical	Calculated	
10	0.1730	0.1718	+0.69
15	0.2588	0.2576	+0.46
20	0.3450	0.3435	+0.44
25	0.4306	0.4288	+0.42
30	0.5172	0.5152	+0.39

IR spectra

(i) *Spectra of ligand:* The infrared spectra of the N- α -naphthyl oxamic acid shows the following important bands: (i) for $>\text{C}=\text{O}$; (ii) $-\text{C}-\text{OH}$. (iii)



$=\text{C}=\text{C}<$; (iv) $-\text{NH}-\underset{|}{\text{C}}=\text{O}$ and (v) for mixed stretching vibrations of $\nu(\text{OH})$ and $\nu(\text{NH})$.

The oxamic acid shows a strong absorption band in the region 3240 cm^{-1} which can be assigned to the mixed stretching vibration of —OH and —NH group. This shows that there is a strong intra and intermolecular hydrogen bonding,¹¹⁻¹³ due to this the actual frequency of —OH bond is lowered.^{14, 15} Another strong absorption band at 1605 cm^{-1} can be assigned to the asymmetric carboxylate ion.¹⁶ —NH— band frequency is observed at 1515 cm^{-1} . This shows the coupling of —NH band with amide bond (—NH—C=O). A broad strong absorption band at 1705 cm^{-1} may be attributed and assigned to the ketonic group —C=O similar to pyruvic acid.

(ii) *IR spectra of complex*: The complex shows a new band in the region 3340 cm^{-1} . The shifting of —NH band frequencies in higher region indicates that —NH bond does not take part in the coordination. The ketonic frequency in the complex is shifted towards lower region 1650 cm^{-1} which was observed in free acid at 1705 cm^{-1} . This shows that oxygen atom of ketonic group participate in coordination. The C=O band of free COOH group in ligand (1605 cm^{-1}) is shifted to 1560 cm^{-1} showing that free COOH group is absent.¹⁷ Vibration of the COO-1 group appears at 1560 and 1430 cm^{-1} respectively with $\Delta\nu$ value indicating that carboxylate acts as a unidentate coordinating agent.¹⁸ Thus the ligand is complex and is acting as bidentate O—O donor, leaving —NH— group free.

ACKNOWLEDGEMENT

The author is thankful to Rajendra Mathur, Assistant Professor of Polymer Science, Department of Chemistry, M.L. Sukhadia University, for full co-operation and interest in the present work.

REFERENCES

1. V.K. Sharma, G.K. Chaturvedi and R.C. Sharma, *Metals and Minerals*, **18**, 171 (1978).
2. _____, *Chemical Era*, **14**, 198 (1978).
3. _____, *Talanta*, **27**, 595 (1980).
4. V.K. Sharma, *Orient. J. Chem.*, **7**, 104 (1991).
5. _____, *Asian J. Chem.*, **4**, 26 (1992).
6. _____, *Orient J. Chem.*, **8**, 46 (1992).
7. _____, *U. Scientist. Phyl. Sciences*, **5**, 98 (1993).
8. I.M. Kolthoff and R. Elmquist, *J. Am. Chem. Soc.*, **53**, 1225 (1931).
9. O.P. Gupta and J.P. Tandon, *J. Inst. of Chemists*, (India) **2**, 169 (1968).
10. G. Schwarzenbach, *Complexometric Titration*, Methuen and Co. Ltd., New York, p. 73 (1960).
11. M.St.C. Fleet, *J. Chem. Soc.*, 1941 (1948).
12. J.W. Baker, M.M. Davies and J. Gaunt, *J. Chem. Soc.*, **24** (1944).
13. G.B.B.M. Sutherland, *Discussion Faraday Soc.*, **9**, 274 (1980).
14. R.E. Richards and J. Thomson, *J. Chem. Soc.*, 1238 (1947).
15. S.T. Darmon and G.B.B.M. Sutherland, *Nature*, **164**, 440 (1949).
16. Wenogard and R.A. Surr, *J. Am. Chem. Soc.*, **79**, 5844 (1957).
17. L.J. Bellamy, *Infra-red Spectra of Complex Molecules*, Methuen and Co. Ltd., London (1964).
18. G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, **33**, 227 (1980).