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CARBON-13 NMR CHEMICAL SHIFTS STUDY IN ZINC AND ANTIMONY OXINATE

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Abstract

Carbon-13 NMR chemical shifts measurements have been carried out on zinc (II) oxinate and antimony (III) oxinate in DMSO-d_6 solution at 22.49 MHz frequency and at 100°C . The spectra are assigned on the basis of previously published proton spectra. Carbon-13 spectra of zinc and antimony oxinates, slightly differ from each other and as well as from that of oxine.

Introduction

The chelating ligand 8-Hydroxyquinoline, 8-Quinolinol or Oxine (I), finds numerous applications in analytical chemistry [1-4]. Oxine and metal oxinates have been subject of various physico-chemical investigations using vide variety of analytical techniques [5-13].

The NMR study of metal oxinates is less reported. However, a detailed proton NMR study of metal oxinates was made by Baker and Sawyer [14]. Later on, carbon-13 chemical shifts of some 4-methyl oxine complexes was carried by Howie et al. [15]. More recently, Engelter et al. [16] have studied the proton NMR of UO_2 (VI), Th (IV) and Sc (III) oxine complexes.

The NMR study of nuclei other than proton is hindered badly because of the solubility of these complexes. The oxine metal complexes are highly insoluble in organic solvents. In inorganic solvents, their decomposition occurs. Solubility is very poor even in a powerful solvent like DMSO-d_6.

The present study is part of the previous work on carbon-13 chemical shifts of these insoluble type of metal oxinates [17].

Experimental

AnalaR grade chemicals obtained from Merck-Germany, were used in this work.

The metal oxinates were prepared in accordance with the standard procedure reported in literature [1,3,8]. These were subjected to elemental analysis, infrared and atomic absorption spectroscopy for purity check and metal content. Yanaco MT-3 CHN corder, Hitachi 260-50 infrared spectrophotometer and Hitachi 180-50 atomic absorption spectrophotometer were used to analyze the samples.

For carbon–13 NMR, zinc (II) and antimony (III) oxinates were dissolved in DMSO–d_6 and solution was then filtered. Samples for NMR, were prepared in 10 mm O.D. Wilmand glass tube and volume was approximately 1.5 ml.

The carbon-13 spectra were recorded on Jeol FX 90Q NMR spectrometer operated in Fourier Transform mode. A multinuclear tunable probe (10 mm) was used and carbon–13 resonance frequency was set at 22.49 MHz. The 90° pulse width was 25 μs. The carbon–13 spectra were recorded with complete proton noise decoupling mode at a frequency of 1 kHz. Because of low solubility, 5,000 accumulations were done on these samples to get better signal to noise ratio.

Results and Discussion

The results for percent carbon, hydrogen, nitrogen and metal in zinc (II) and antimony (III) oxinate are given in Table 1. They are in conformity with the theoretical values. The infrared spectra are also in agreement with the standard spectra.

The carbon–13 spectrum of the parent compound oxine is shown in Figure 1. It was recorded in $CDCl_3$ at the room temperature.

The carbon-13 spectra of zinc (II) oxinate and antimony (III) oxinate are shown in Figures 2 and 3. These were recorded at 100°C and after 5,000 accumulations. The peaks were assigned on the basis of proton spectra [14]. The

chemical shifts were assigned relative to methyl peak of DMSO-d_6. These were then corrected relative to TMS, used as an internal standard.

The data for proton and carbon-13 chemical shifts are presented in Table 2. From the spectra and data, it is observed that the carbon-13 spectra of $Zn(Ox)_2$ (Figure 2) and Sb $(Ox)_3$ (Figure 3) slightly differ from each other and as well as from the parent compound oxine (Figure 1). However, the spectrum for zinc (II) oxinate is more noisy as compared to the spectrum of antimony (III) oxinate. This is probably due to the low solubility of the zinc oxinate.

The different structure of the divalent and trivalent metal oxinates, poses some problems in their solubility, proton and carbon-13 spectra. At higher temperature, the solubility may be increased and the spectra may be less noisy. In the light of these results, a detailed variable and high temperature study will be carried out on the metal oxinates.

Table 1

Percent Carbon, Hydrogen, Nitrogen and Metal in Zinc (II) Oxinate and Antimony (III) Oxinate

Metal Oxinate	% Carbon	% Hydrogen	% Nitrogen	% Metal
$Zn(C_9H_6NO)_2.H_2O$	58.05 (58.10)	3.75 (3.77)	7.60 (7.53)	17.56 (17.60)
$Sb(C_9H_6NO)_3$	58.41 (58.44)	3.20 (3.25)	7.56 (7.57)	21.93 (21.96)

Figures in parentheis denote theoretical percent.

Table 2

Proton and Carbon-13 Chemical Shifts in Oxine, Zinc (II) Oxinate and Antimony (III) Oxinate

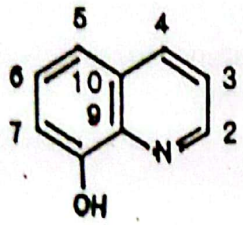
Carbon* Number	Proton Chemical Shift#			Carbon-13 Chemical Shift**		
	Oxine	$Zn(Ox)_2$	$Sb(Ox)_3$	Oxine	$Zn(Ox)_2$	$Sb(Ox)_3$
2	9.11	8.79		148.00	144.71	143.31
3	7.78	7.68		121.80	125.58	121.47
4	8.55	8.57		136.00	130.10	130.10
5	7.66	7.26		117.70	120.86	110.75
6	7.71	7.56		127.40	129.18	128.60

Carbon* Number	Proton Chemical Shift#			Carbon-13 Chemical Shift**		
	Oxine	$Zn(Ox)_2$	$Sb(Ox)_3$	Oxine	$Zn(Ox)_2$	$Sb(Ox)_3$
7	7.42	7.17		111.20	111.54	99.96
8	—	—		153.30	161.64	158.37
9	—	—		138.50	139.58	139.14
10.	—	—		128.70	129.50	128.57

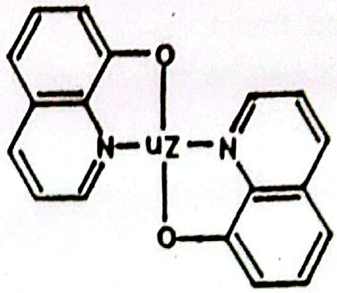
* Carbon atom numbering is according to Structure (I) given in text.

\# Reference 14. These values were given relative to DMSO-d_6 protons. Here these are converted relative to TMS.

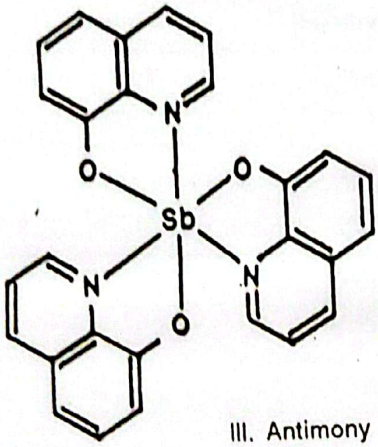
** Present study is in DMSO-d_6. TMS was used as an internal standard. Oxine was dissolved in $CDCl_3$.



I: 8-Hydroxyquinoline, 8-Quinolinol or Oxine.



II: Zinc (II) Oxinate.



III. Antimony (III) Oxinate.

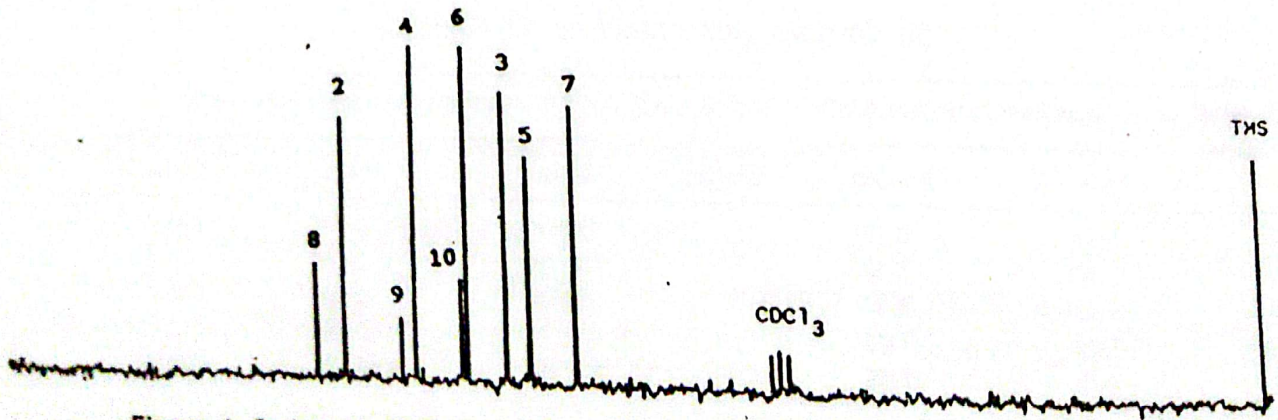


Figure 1 Carbon-13 NMR Spectrum of Oxine in $CDCl_3$ at Room Temperature.

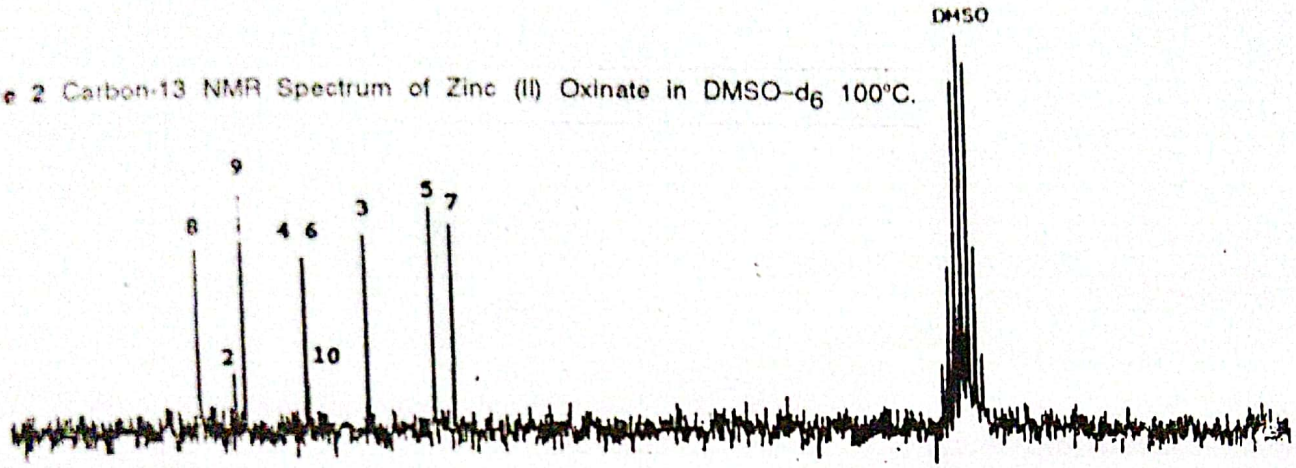


Figure 2 Carbon-13 NMR Spectrum of Zinc (II) Oxinate in DMSO-d_6 100°C.

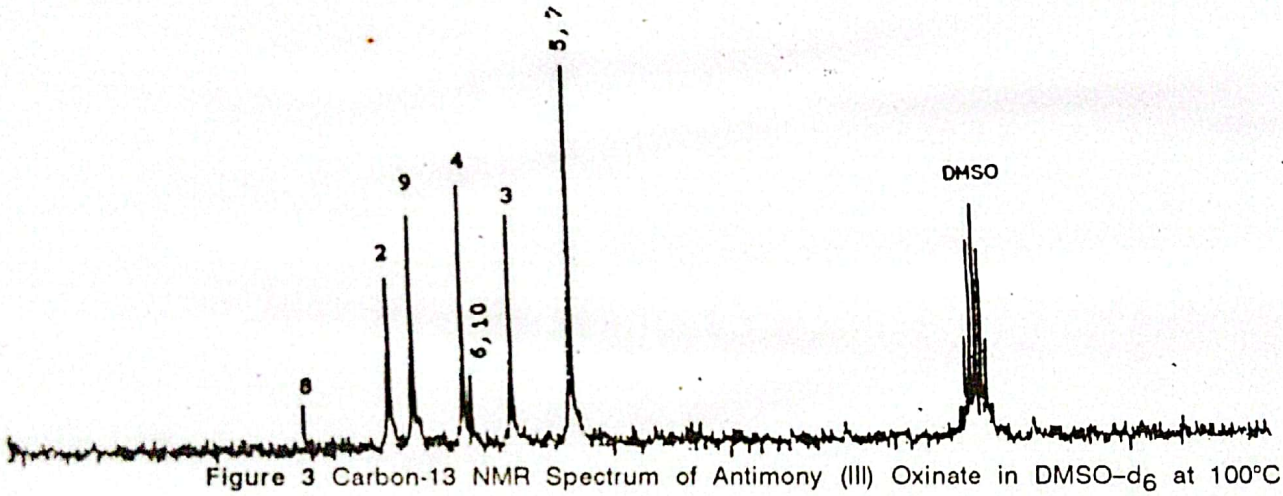


Figure 3 Carbon-13 NMR Spectrum of Antimony (III) Oxinate in DMSO-d_6 at 100°C.

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