

Triethylene Tetramine and Diethylene Triamine Based Schiff Base Complexes of Cerium(IV)

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Schiff base complexes of Ce(IV) formed from salicylaldehyde/acetophenone and L = triethylene tetramine (trien)/diethylene triamine (dien) namely $[\text{Ce}_2(\text{L-4H})(\text{CHC}_6\text{H}_4\text{O})_2(\text{C}_2\text{O}_4)_3] \cdot x\text{H}_2\text{O}$ $x = 1$ or 2 , $[\text{Ce}_2(\text{L-4H})(\text{CCH}_3\text{C}_6\text{H}_5)_2(\text{C}_2\text{O}_4)_3(\text{OH})_2] \cdot \text{H}_2\text{O}$ are reported. The complexes have been characterized by elemental and thermal analysis, magnetic and conductivity studies, IR, NMR and UV-visible spectroscopic studies. Some of the complexes show promising antibacterial activity against *Bacillus subtilis*, *Streptococcus mutans*, *E. coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

Key Words: Ce(IV) trien salicylaldehyde/acetophenone Schiff bases, Ce(IV) dien salicylaldehyde/acetophenone Schiff bases, Antibacterial studies.

INTRODUCTION

The study of Schiff base complexes of metals is eternal and draws the attention of scientists of all time due to a variety of applications in biological, clinical, analytical and pharmacological areas¹⁻³. Schiff base complexes of vanadium have been explored to have some catalytic application in electro reduction of oxygen to water, a reaction of very high significance⁴. Schiff base complexes of uranyl ion gain attention due to their luminescence properties⁵. It is believed that titanium and molybdenum Schiff base complexes may turn potential systems for *in vitro* nitrogen fixation. Cerium is a commonly available lanthanide metal, which is extensively used in several fields like glass manufacture, petroleum refining, storage of H₂ and O₂, organic synthesis etc. However not much has been done on the potential of cerium compounds in biological field. Here we report the isolation, characterization and antibacterial studies on diethylene triamine (dien) and triethylene tetramine (trien) based Schiff base complexes of Ce(IV).

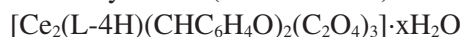
EXPERIMENTAL

The salicylaldehyde Schiff base complexes may be prepared by adding simultaneously 0.03 mol of ammonium oxalate, 0.01 mol of trien/dien and 0.02 mol of salicylaldehyde to 0.02 mol of ceric ammonium nitrate in water with constant stirring which is continued for 0.5 h. Similarly, the acetophenone complexes may prepared by adding simultaneously 0.03 mol of ammonium oxalate, 0.01 mol of trien/dien and 0.02 mol of acetophenone to 0.02 mol of ceric ammonium nitrate in water with

constant stirring. Then added 5 mL of dilute NaOH solution and continued stirring for 0.5 h. The acetophenone complex was yellow solids while salicylaldehyde complex was brown. Complexes were filtered and dried in air. Cerium in the complex was determined gravimetrically as CeO₂ and nitrogen is estimated by Kjeldhal's method. TG/DTA were recorded in nitrogen atmosphere using Netzschsta 409 C/CD thermal analyzer with a heating rate of 10 °C/min. Magnetic susceptibility studies were carried out using vibrating magnetometer EG and GPARC model 155. UV-Visible absorption spectra were recorded as mull using Varian Cary Spectrophotometer 5E-UV-vis-NIR. IR Spectra were recorded in KBr using Bruker IFS 66V FT IR spectrometer. Conductivity of the soluble complexes were measured using simple conductivity bridge. Antibacterial activity of the complexes were tested using minimum modification of the disc diffusion method⁶.

RESULTS AND DISCUSSION

Elemental and thermal analysis data (Tables 1 and 2) confirmed the compositions:



where $x = 2$, L = trien and $x = 1$, L = dien for salicylaldehyde complexes and



where L = dien/trien for the acetophenone complexes.

TABLE-1
ELEMENTAL ANALYSIS DATA OF THE Ce(IV) COMPLEXES

Complexes	Colour	Metal (%)		Nitrogen (%)		Λ_{max} (nm)
		Exp.	Theo.	Exp.	Theo.	
$[\text{Ce}_2(\text{L-4H})(\text{CHC}_6\text{H}_4\text{O})_2(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$, L = trien	Brown	29.31	30.06	6.97	6.01	325, 360
$[\text{Ce}_2(\text{L-4H})(\text{CCH}_3\text{C}_6\text{H}_5)_2(\text{C}_2\text{O}_4)_3(\text{OH})_2] \cdot \text{H}_2\text{O}$, L = trien	Yellow	30.56	29.61	6.31	5.92	383, 400
$[\text{Ce}_2(\text{L-4H})(\text{CHC}_6\text{H}_4\text{O})_2(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$, L = dien	Brown	32.56	32.16	5.22	4.82	320, 360
$[\text{Ce}_2(\text{L-4H})(\text{CCH}_3\text{C}_6\text{H}_5)_2(\text{C}_2\text{O}_4)_3(\text{OH})_2] \cdot \text{H}_2\text{O}$, L = dien	Yellow	31.92	31.02	4.16	4.65	300, 328, 360

The salicylaldehyde complexes are highly soluble in DMSO while acetophenone complexes are less soluble. The TG/DTA data on complexes indicate less thermal stability with loss of water and an oxalate unit in the first stage of decomposition. Loss of water is accompanied by an endotherm, while subsequent loss of oxalate group leads to an exothermic peak. This stage is followed by further decomposition of the ligand leading to CeO₂ formation. The complexes exhibit negative magnetic susceptibility values indicating diamagnetic nature. The molar conductance of the complexes range from 1-2 ohms⁻¹ cm²/mol indicating non-electrolytic nature. The electronic spectral data (Table-1) indicate absorptions only in the range 300-400 nm, characteristic of Ce(IV) complexes. The IR spectra of the complexes (Table-3) show broad absorptions corresponding to OH and NH stretching in the regions 3455-3350 and 3250-3075 cm⁻¹, respectively. $\nu_{\text{as}}(\text{COO}^-)$ of the oxalate group merges

TABLE-2
TGA AND DTA DATA ON TRIEN AND DIEN COMPLEXES

Complexes	% Water + oxalate loss (stage-1)		CeO ₂ (%)		DTA Peaks stage-1	DTA Peaks stage-2
	Exp.	Theo.	Exp.	Theo.		
[Ce ₂ (L-4H)(CHC ₆ H ₄ O) ₂ (C ₂ O ₄) ₃ ·2H ₂ O, L = trien	13.00	13.30	36.00	36.93	53(-), 101.6(+)	315.8-, 400.1+
[Ce ₂ (L-4H)(CCH ₃ C ₆ H ₅) ₂ (C ₂ O ₄) ₃ (OH) ₂ ·H ₂ O, L = trien	11.00	11.20	39.12	36.38	78(-), 140.6(+)	315.8-, 400.9+, 1063.9+
[Ce ₂ (L-4H)(CHC ₆ H ₄ O) ₂ (C ₂ O ₄) ₃ ·H ₂ O, L = dien	11.00	12.16	40.00	39.50	95(-), 125.5(+)	305.0-, 342+, 400+, 559+
[Ce ₂ (L-4H)(CCH ₃ C ₆ H ₅) ₂ (C ₂ O ₄) ₃ (OH) ₂ ·H ₂ O, L = dien	12.00	11.73	40.41	38.11	58(-), 100.4(+)	262.0-, 398.4+, 484.2-, 936.8+

Endotherm (-), exotherm (+)

with C=N and appears as a very strong band around 1630 cm⁻¹. The vibrations characteristic of the benzene ring appears in the region 1535-1415 cm⁻¹. NMR data on salicylaldehyde complexes (Table-4) show NH protons around 8.5 ppm and aromatic protons as multiplets due to *ortho* substitution in the range 7.20-7.65 ppm. The CH=N proton appears around 6.8-6.9 ppm. The CH₂ protons are seen at 2.46 and 2.52 ppm in the trien and dien complexes. Antibacterial activities of salicylaldehyde trien schiff base complex and salicylaldehyde dien Schiff base complex (Table-5) show that the complexes are active against all the five bacterias namely *Bacillus subtilis*, *Streptococcus mutans*, *E. coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*. 15-25 µg of sample have been used for each bacterial study. As the concentration of the complex increases, it is seen that the diameter of the inhibitory zone also increases indicating an increased activity. The trien complex

TABLE-3
IR SPECTRAL DATA (cm⁻¹) ON TRIEN AND DIEN COMPLEXES OF Ce(IV)

Complexes	v(OH)	v(NH)	v(CH) aromatic	v(CH) aliphatic	v(COO ⁻) oxalate + (CN)	Ring stretching
[Ce ₂ (L-4H)(CHC ₆ H ₄ O) ₂ (C ₂ O ₄) ₃ ·2H ₂ O, L = trien	3350	3188, 3078	3031	2984, 2875	1625	1531, 1461
[Ce ₂ (L-4H)(CCH ₃ C ₆ H ₅) ₂ (C ₂ O ₄) ₃ (OH) ₂ ·H ₂ O, L = trien	3434	3250, 3116	3074	2923, 2853	1626	1464, 1453
[Ce ₂ (L-4H)(CHC ₆ H ₄ O) ₂ (C ₂ O ₄) ₃ ·H ₂ O, L = dien	3391	3266	3031, 3063	2953, 2859	1631	1520, 1468, 1428
[Ce ₂ (L-4H)(CCH ₃ C ₆ H ₅) ₂ (C ₂ O ₄) ₃ (OH) ₂ ·H ₂ O, L = dien	3421	3249, 3146	3015	2984, 2859	1625	1512, 1437

TABLE-4
NMR SPECTRAL DATA ON COMPLEXES

Chemical shift (ppm)		Assignments
$[\text{Ce}_2(\text{L-4H})(\text{CHC}_6\text{H}_4\text{O})_2(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$ (L = trien)	$[\text{Ce}_2(\text{L-4H})(\text{CHC}_6\text{H}_4\text{O})_2(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$ (L = dien)	
8.4430	8.6983	NH protons
7.2899	7.6654, 7.4606	Aromatic protons
6.8206	6.9133	CH=N proton
2.4599	2.5181	CH ₂ protons

TABLE-5
ANTIBACTERIAL STUDIES

Organisms	Diameter of inhibitory zone (mm)					
	$[\text{Ce}_2(\text{L-4H})(\text{CHC}_6\text{H}_4\text{O})_2(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$ L = trien			$[\text{Ce}_2(\text{L-4H})(\text{CHC}_6\text{H}_4\text{O})_2(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$ L = dien		
	15 µg	20 µg	25 µg	15 µg	20 µg	25 µg
<i>S. aureus</i>	7	9	12	8	10	12
<i>B. subtilis</i>	16	18	20	12	14	16
<i>S. mutans</i>	9	11	13	8	9	11
<i>E. coli</i>	10	10	12	8	10	13
<i>P. aeruginosa</i>	8	9	10	13	14	15

shows maximum activity against *Bacillus subtilis*, while the dien show maximum activity against *Bacillus subtilis* and *Pseudomonas aeruginosa*.

The trien complexes are thus assigned a structure with one cerium coordinated to the four N atoms of trien and O⁻ of salicylaldehyde group and the other cerium chelated by two oxalato groups. The third oxalato group perhaps bridges the two cerium atoms. The dien complexes are assigned a structure with one cerium coordinated to two N atoms of N=C (Schiff base) and two OH groups, while the other cerium is chelated by two oxalato groups. The third oxalato group bridges the two cerium atoms.

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