



Spectroscopic Characterization of Some Oxovanadium(IV, V) Complexes

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Six new oxovanadium(IV, V) complexes of *N*-bis(caproyl)hydroxamic acid, *N*-caproyl acetohydroxamic acids and *N*-caproyl benzohydroxamic acids have been synthesized. The synthesized hydroxamic acids and their oxovanadium(IV, V) complexes were characterized by melting point, running TLC for single spot, elemental analysis, IR, ¹H NMR and electronic spectral studies. The spectral studies suggest distorted octahedral geometry for both V(IV) and V(V) metal complexes.

Keywords: Oxovanadium(IV, V), Distorted octahedral.

INTRODUCTION

In the current decade considerable interest has been focused on the hydroxamic acids, which has been known to possess a broad spectrum of biological activities such as anti-bacterial, antifungal¹, antibiotics², anticancer³ and antioxidant⁴. They are also acquiring much significance as analytical reagents for solvent extraction⁵, liquid-liquid extraction⁶, froth flotation⁷, stabilizers of photographic developing solutions⁸ and spectrophotometer titrations of several metal ions⁹. The biological importance of the vanadium on a triple level, nutritional, pharmacological and toxicological effects are determined by performing a large scale investigation of medicinal plants about their vanadium content and evaluation of the extraction ratio of this element on the herbal teas¹⁰. The no. of patients with diabetes mellitus (DM) is fastly increasing and it was approximately 250 million worldwide in the last decade¹¹. Diabetes mellitus is a disease that results in the chronic hyperglycemia due to an absolute or partial lack of insulin which in turn impairs the glucose, protein and lipid metabolism and ultimately causes several secondary complication¹². Insulin is a signaling hormone which is essential for the metabolism of both carbohydrate and fat. The increased insulin level normally promotes glucose uptake by the liver, gut and peripheral tissues that results in energy production and storage as required by the organism¹³. During the past two decades Se, Cr, Mn, Mo, W, V and Zn ions have been reported to show insulin like effects^{14,15}. Vanadium compounds however, have been proved to be one of the most efficient. A good number of vanadium(IV,V) complexes have been prepared and tested for

antidiabetic agents¹⁶. These facts have prompted us to synthesize new hydroxamic acids and their vanadium(IV, V) metal complexes, which is an extension of our previously reported work^{17,18}.

EXPERIMENTAL

Synthesis of *N*-bis(caproyl)hydroxamic acid (NBCHA): Finely powdered hydroxylamine hydrochloride [0.694 g, 0.01 mol] dissolved in 15 mL distilled water was mixed with 10 mL aqueous solution of [0.40 g, 0.01 M] sodium hydroxide. This mixture was stirred by a mechanical stirrer at 0 °C using external freezing. Then, ethereal solution of [2.75 mL, 0.02 mol] caproyl chloride was added slowly to the above solution for 1.5 h with constant stirring until precipitate was obtained. The obtained crude product was again dissolved in methanol, filtered and dried over anhydrous CaCl₂ under reduced pressure in vacuum desiccators. Similarly, *N*-caproyl acetohydroxamic acid (NCAHA) and *N*-caproyl benzohydroxamic acid (NCBHA) were also synthesized by adding 1:1 molar ratio of caproyl chloride and benzoyl/acetyl chloride respectively.

Synthesis of metal complexes

Synthesis of vanadium(IV) metal complexes: 0.005 mol NBCHA/NCAHA/NCBHA were dissolved in 20 mL deionized water and then nitrogen gas was bubbled through this solution for 15 min with constant stirring. Then, 0.0025 mol vanadyl sulphate dissolved in 15 mL deionized water was added and allowed to react for 45-60 min with the nitrogen gas bubbling at room temperature. Coloured solid products

were obtained which were dried at room temperature and finally in a desiccator over anhydrous CaCl_2 .

Synthesis of vanadium(V) metal complexes: 0.005 mol NBCHA/NCAHA/NCBHA were dissolved in 20 mL deionized water and then nitrogen gas was bubbled through this solution for 15 min with constant stirring. Then, 0.0025 mol ammonium metavanadate dissolved in 15 mL concentrated HCl was added and allowed to react for 45-60 min with the nitrogen gas bubbling at room temperature. Coloured solid products were obtained which were dried at room temperature and finally in a desiccator over anhydrous CaCl_2 .

Physical and analytical measurements: The hydroxamic acids and their metal complexes were analyzed for C, H and N by using micro analyzer technique on Thomas CH-analyzer-35-Carlo Erba-1106 and Coleman-N-analyzer at CDRI Lucknow. IR spectra were recorded in the range of 4000-400 cm^{-1} Perkin Elmer spectrophotometer model Rx1 using KBr pellets. ^1H NMR spectra were recorded on NMR spectrometer Bruker DRX-300 (300 MHz FT-NMR with low and high temperature facility -90°C to $+80^\circ\text{C}$) at SAIF, CDRI, Lucknow. Electronic spectra were recorded on UV 6000 spectrophotometer at SAIF, Chandigarh.

RESULTS AND DISCUSSION

Physical and analytical data of hydroxamic acids and their vanadium metal (IV,V) complexes are presented in Table-1. All the complexes were found coloured and stable at room temperature. In the IR spectra of hydroxamic acids an absorption peak in the region 3468-3417 cm^{-1} is appeared which may be attributed to N-OH stretching vibration. This band has disappeared in the IR spectra of metal complexes indicating the coordination of the ligand to the metal ion through hydroxyl group *via* deprotonation¹⁹. An absorption band in the region 2957-2841 cm^{-1} appears in the IR spectra of hydroxamic acids and their metal complexes which may be attributed to the C-H stretching vibrations of polymethylene linkage. The carbonyl

stretching vibration observed in the region 1688-1675 cm^{-1} in the IR spectra of hydroxamic acids²⁰⁻²². This band has shifted towards lower region by 40-30 cm^{-1} in the case of metal complexes which clearly indicates the co-ordination of the ligands to the metal ion through oxygen atom of carbonyl group. In the infrared spectra of hydroxamic acids and their metal complexes an absorption band in the region 1372-1315 cm^{-1} appears which may be attributed to C-N stretching vibrations²³⁻²⁵. A medium sharp intensity band in the region 1160-1114 cm^{-1} is observed in the infra-red spectra of hydroxamic acids and their metal complexes which may be attributed due to stretching vibrations of -N-O group²⁶⁻³⁰. In the IR spectra of vanadium(IV) metal complexes a medium sharp intensity band in the region 969-985 cm^{-1} is obtained which may be attributed due to V=O stretching vibrations whereas in the IR spectra of vanadium(V) metal complexes a band in the region 963.2-941.4 cm^{-1} has appeared which may be due to VOCl stretching vibrations³¹⁻³³. Two bands in the region 3479- 3405 cm^{-1} and 922-809 cm^{-1} are observed in the infrared spectra of all metal complexes which indicate the presence of coordinated water molecule in the co-ordination sphere. All complexes exhibited a new band in the region 470-460 cm^{-1} which may be attributed due to the formation of V-O bonds^{34,35}. Appearance of this band further confirms the coordination of carbonyl group and oxygen of hydroxyl group *via* deprotonation of ligand with the metal ions.

The synthesized hydroxamic acids exhibited a singlet in the range of δ 10.339-10.889 ppm due to NOH proton. Ligand NBCHA exhibited two triplet one in the range δ 0.818-0.862 ppm due to $-\text{CH}_3$ protons of $-\text{CH}_2\text{CH}_3$ moiety and other in the range δ 2.978-3.203 ppm due to COCH_2 protons. Two multiplets appeared, one in the range δ 1.361-1.512 ppm due to polymethylene protons and second in the range δ 1.873-2.019 ppm due to two protons of $-\text{CH}_2-$ of $-\text{CH}_2\text{CH}_3$ moiety. Ligand NCAHA has shown singlet at δ 3.410 ppm due to three protons of CH_3 of $-\text{COCH}_3$ moiety. Two triplet appear one in the range

TABLE-1
PHYSICAL PROPERTIES AND PERCENTAGE COMPOSITION OF SYNTHESIZED HYDROXAMIC ACIDS AND THEIR METAL COMPLEXES

Compound	m.f.	Colour	Elemental analysis (%): Found (Calcd.)						m.p./decomposition temp. ($\pm 2^\circ\text{C}$)
			M	C	H	N	S	Cl	
NBCHA	$\text{C}_{12}\text{H}_{23}\text{NO}_3$	Brown	–	62.88 (63.00)	10.04 (9.87)	6.11 (6.00)	–	–	120
NCAHA	$\text{C}_8\text{H}_{15}\text{NO}_3$	Creamish	–	55.49 (55.61)	8.67 (8.42)	8.09 (7.87)	–	–	115
NCBHA	$\text{C}_{13}\text{H}_{17}\text{NO}_3$	Light brown	–	66.38 (66.42)	7.23 (7.11)	6.38 (6.14)	–	–	120
[V(IV)NBCHA]	$[\text{V}(\text{IV})\text{O}(\text{C}_{12}\text{H}_{22}\text{NO}_3)_2 \cdot \text{H}_2\text{O}]\text{SO}_4$	Dark purple black	8.01 (7.88)	45.21 (45.46)	7.22 (7.00)	4.39 (4.12)	5.02 (4.88)	–	118
[V(IV)NCAHA]	$[\text{V}(\text{IV})\text{O}(\text{C}_8\text{H}_{14}\text{NO}_3)_2 \cdot \text{H}_2\text{O}]\text{SO}_4$	Purple black	9.71 (9.50)	36.57 (36.63)	5.71 (5.53)	5.33 (5.14)	6.01 (5.91)	–	120
[V(IV)NCBHA]	$[\text{V}(\text{IV})\text{O}(\text{C}_{13}\text{H}_{16}\text{NO}_3)_2 \cdot \text{H}_2\text{O}]\text{SO}_4$	Dark purple black	7.86 (7.62)	48.07 (48.44)	5.24 (5.10)	4.31 (4.18)	4.93 (4.76)	–	120
[V(V)NBCHA]	$[\text{V}(\text{V})\text{OCl}(\text{C}_{12}\text{H}_{22}\text{NO}_3)_2 \cdot \text{H}_2\text{O}]\text{Cl}_2$	Dark purple black	7.88 (7.71)	44.48 (44.59)	7.10 (6.94)	4.32 (4.11)	–	10.96 (10.87)	118
[V(V)NCAHA]	$[\text{V}(\text{V})\text{OCl}(\text{C}_8\text{H}_{14}\text{NO}_3)_2 \cdot \text{H}_2\text{O}]\text{Cl}_2$	Purple black	9.52 (9.27)	35.85 (35.97)	5.60 (5.48)	5.23 (4.97)	–	13.26 (13.00)	118
[V(V)NCBHA]	$[\text{V}(\text{V})\text{OCl}(\text{C}_{13}\text{H}_{16}\text{NO}_3)_2 \cdot \text{H}_2\text{O}]\text{Cl}_2$	Dark purple black	7.73 (7.57)	47.30 (47.59)	5.15 (5.01)	4.25 (4.13)	–	10.76 (10.63)	120

NBCHA = N-bis(caproyl)hydroxamic acid; NCAHA = N-caproyl acetohydroxamic acid; NCBHA = N-caproyl benzohydroxamic acid

δ 0.826-0.851 ppm due to CH_3 protons of $-\text{CH}_2\text{CH}_3$ moiety and second appeared in the range δ 2.981-3.206 ppm due to $-\text{COCH}_2$ protons. Two multiplets appeared one in the range δ 1.228-1.517 ppm due to polymethylene protons and second in the range δ 1.877-2.021 ppm due to $-\text{COCH}_2$ protons. Ligand NCBHA exhibited one multiplet in the range δ 1.914-2.050 ppm due to polymethylene protons. The another multiplets appeared in the range 3.031-3.166 ppm due to $-\text{CH}_2$ protons of polymethylene linkage and multiplets due to aromatic protons in the range δ 7.411-7.503 ppm. Two triplets one appeared at δ 1.914-1.962 ppm due to $-\text{CH}_3$ protons and second appears at δ 2.668-2.716 ppm due to COCH_2 protons.

The electronic spectra of vanadium(IV) complexes exhibited three bands in the region $13440\text{--}12940\text{ cm}^{-1}$, $16550\text{--}16129\text{ cm}^{-1}$, $24650\text{--}23150\text{ cm}^{-1}$ corresponding to the transitions ${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_g$, ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$, ${}^2\text{B}_{2g} \rightarrow {}^2\text{A}_{1g}$ respectively which suggest distorted octahedral geometry³⁶ for these complexes. However, as expected the vanadium(V) complexes do not show significant bands in their electronic spectra due to diamagnetic nature of vanadium(V).

On the basis of elemental analysis and spectral studies, it is suggested that all the V(IV) and V(V) metal complexes of hydroxamic acids have distorted octahedral geometry as presented in the Figs. 1 and 2.

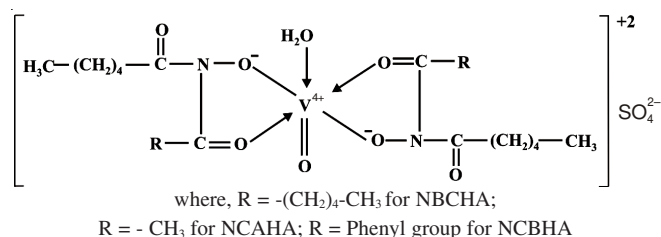


Fig. 1. Vanadium(IV) metal complexes of hydroxamic acids

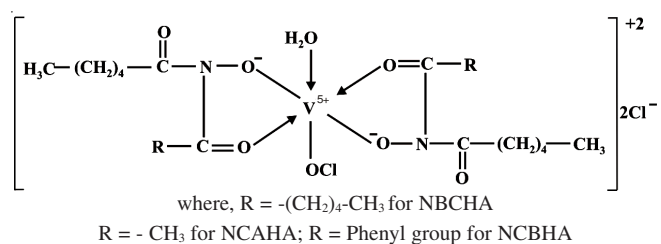


Fig. 2. Vanadium(V) metal complexes of hydroxamic acids

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