



Biocoordination behavior of oxovanadium with streptomycin, tetracycline and oxime containing (n, o) donor atoms mixed ligands. synthesis, spectral characterisation xrpd and molecular structure of the complexes

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ABSTRACT

To understand complexation behavior of antibiotics, such streptomycin, tetracycline and oxime with studied oxovanadium coordination to novel ligands by various spectroscopic techniques. The crystal system, lattice parameters, unit cell, particle size and volume have been determined by X-ray powder diffraction data. The geometries of the complexes have been optimized on the basis of molecular modeling. Spectroscopic data indicates deprotonation & coordination of the secondary alcoholic OH and NH₂ groups with oxovanadium. Mass spectrum explains the successive degradation of the molecular species in solution and justifies ML complexes. The crystal data: complex I is monoclinic crystal system space group $P_{21/M}$, $a = 14.4998(\text{\AA})$, $b = 5.9531(\text{\AA})$, $c = 4.4909(\text{\AA})$, $\alpha = 90.00^\circ$, $\beta = 96.29^\circ$, $\gamma = 90.00^\circ$, $V = 385.44 \text{\AA}^3$; complex II is tetragonal crystal system, space group $P_{4/mmp}$, $a = 12.6313(\text{\AA})$, $b = 12.6313(\text{\AA})$, $c = 6.3494(\text{\AA})$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, $V = 1013.06 \text{\AA}^3$. Molecular structures of the complexes have been optimized by MM2 calculations and supported octahedral arrangements in both complexes.

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Introduction

Oxovanadium complexes especially with bi- and tridentate chelating ligand to the metal mainly via oxygen and nitrogen atoms, have been extensively investigated in recent years with respect to their remarkable efficiency as antibiotic mimetic compounds [1-4]. Their use as orally active and intravenous medicaments would represent an important advance in the treatment of human anticancer, antituberculosis. Other studies involving potential applications of oxovanadium complexes have been also performed with emphasis for example, in their antitumor [5] and antimalarial [6] activity. As many organic antibiotics have been used in medicine do not have a purely organic mode of action some activated or biotransformed by oxovanadium, others have a direct or indirect effect on metal ion metabolism. Vanadium compounds show interesting biological and pharmacological properties [6-9]. Many have insulin-mimetic activities while others possess antitumoral effects. In vertebrates, once the vanadium compounds are absorbed, they are distributed among tissues and accumulate in bones, liver and kidney. Even though some simple vanadium species have beneficial biological properties, development of new vanadium derivatives with synthesized mixed ligands using streptomycin, tetracycline and oxime to improve the bioavailability [10-15] and decrease the side effects is needed.

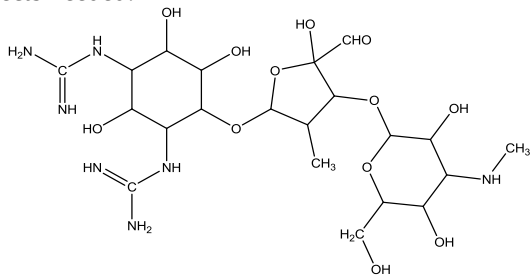


Figure 1. Graphical structure of streptomycin

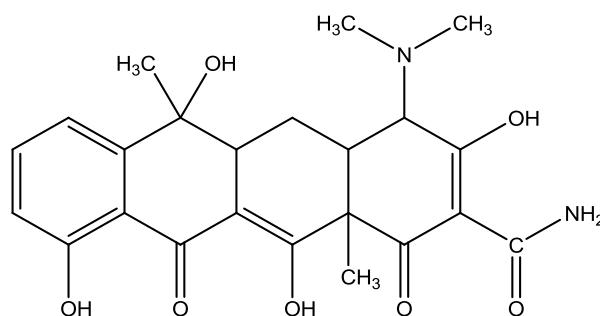


Figure 2. Graphical structure of tetracycline

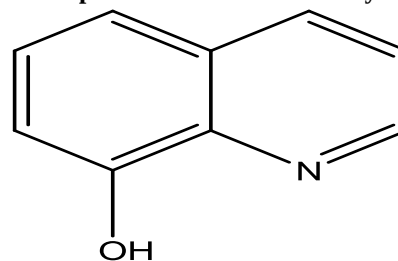


Figure 3. Structure of oxime

This particular article is focused on the twin areas of metalloorganic and oxovanadium coordination chemistry. The organic framework is a mixed ligand, which has various applications in industry and medicine [16-19]. The coordination chemistry of oxovanadium is disproportionately sparse when compared with earlier reports [20-21]. The coordination abilities of nitrogen and oxygen donor atoms are used in the present study and described with spectroscopic characterization techniques. The bond formation between oxovanadium and the asymmetric ligand is detected, studied and explored by various spectroscopic techniques, molecular modeling and XRPD studies. The ligand used is shown in figure 1, 2, 3, as mixed ligands.

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Material and methodology

All the chemicals used in this study were of analytical grade which obtained from Merck. Streptomycin, tetracycline and oxime were purchased from Sigma Aldrich, USA. Solvents used were of analytical grade and were purified by standard procedures. The stoichiometric analyses (C, H and N) of the complexes were performed using Elementar vario EL III (Germany) model. Metal contents were estimated on an AA-640-13 Shimadzu flame atomic absorption spectrophotometer in solution prepared by decomposing the respective complex in hot concentrated HNO_3 . Their IR spectra were recorded on Perkins–Elmer FTIR spectrophotometer in KBr and polyethylene pellets. The electronic spectra were recorded in water on Beckman DU-64 spectrophotometer with quartz cells of 1 cm path length. ^1H NMR spectra were recorded in $\text{DMSO}-d_6$ solvent on a Bruker Advance 400 instrument. The XRD powder pattern were recorded on a vertical type Philips 1130/00 X-ray diffractometer, operated at 40 kV and 50 Ma generator using the $\text{CuK}\alpha$ line at $1.54056 \text{ \AA}$ as the radiation sources. Sample was scanned between 5° to $70^\circ(2\theta)$ at 5°C . The crystallographic data was analyzed by using the CRYSFIRE –2000 powder indexing software package and the space group was found by the CHECK CELL program. Debye – Scherer relation with the help of 100% peak width determined the particle size. The experimental density was determined by Archimedes method. Rigaku model 8150 thermal analyzer (Theraflex) was used for the simultaneous recording of TG-DTA curves at a heating rate of 5° min^{-1} . For the TG, the instrument was calibration was done using calcium oxalate while for DTA calibration was done using indium metal, both of which were supplied along with the instrument. A flat bed type alumina crucible was used with α -alumina (99% pure) as the reference materials for DTA. The number of decomposition step was identified using TG. The activation energy and Arrhenius constant of the degradation process was obtained by Coats and Redfern method.

3D - Molecular modeling

3D molecular modeling of the proposed structure of the complexes was performed using CsChem3D Ultra -12 program package. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries. The optimized structures of the complexes were performed by MM2 programme contained CS chem. Office programme. The potential energy of the molecule was the sum of the following terms: $E = E_{\text{str}} + E_{\text{ang}} + E_{\text{tor}} + E_{\text{vdw}} + E_{\text{oop}} + E_{\text{ele}}$. Where all E's represent the energy values corresponding to the given types of interaction. The subscripts str, ang, tor, vdw, oop and ele denote bond stretching, angle bonding, torsion deformation, van der waals interactions, out of plane bending and electronic interaction, respectively.

Synthesis of complex

To 50 mL of 0.2 M aqueous solution of VOCl_2 , 100 mL of (0.1M) 1:1 of streptomycin and oxime in 50% ethanol in a cleaned round bottom flask and stirred 2 hours with maintained the pH 2.5-4.0. This solution was purified by standard procedure [22]. Dried this solution at room temperature to get good crystalline solid of the complex 1. And followed the same process for the complex 2 by using tetracycline and oxime (1:1M) as a ligand with VOCl_2 .

RESULTS and discussions

Elemental analysis

Satisfactory results of elemental analysis (Table 1) and spectral studies revealed that the complexes were of good purity. Various attempts to obtain the single crystals have so far been

unsuccessful. X-ray diffraction studies indicate crystalline nature of the metal complexes. The complexes were soluble in polar solvents.

Vibrational Spectra

Novel ligand exhibits absorptions 3425 of OH group, 2928 of NH_2 , 1507 OH, 1223 and 781 cm^{-1} . strong band of primary OH and NH of oxime. These bands are very metal complexes indicating non – involvement of the oxygen atoms of hydroxyl group in coordination with the metal ions [23]. The stretching frequencies of ligand hydroxyl and give bands at 3268 and 3522 cm^{-1} with a shoulder at about 3550 cm^{-1} . These bands appear in the complexes as strong band absorption in the region 3420 – 3445 cm^{-1} . These bands appear for the new complex at the same wave number, ruling out the participation of hydroxyl oxygen in the coordination. These results confirm that complexation occurred and suggest that the oxygen of the hydroxyl group is involved in the coordination sphere in both complexes [24]. The vibrational bands due to rocking & wagging modes of water and metal – oxygen stretching modes are observed in the 825 – 350 cm^{-1} region for all the complexes may be attributed to coordinated water [25]. This can be confirmed with the help of thermograms. A new band in the 600 – 300 cm^{-1} regions in the spectra of the complexes is assignable to $\nu(\text{M} - \text{O})$.

^1H NMR

The ^1H NMR spectra of the streptomycin complexes of oxovanadium in a $\text{DMSO}-d_6$ solvent of the ligand and M-ligand complex show well-resolved signals Figure 4. ^1H NMR spectrum of complex (I). The N-H protons of amine, which would have undergone very rapid exchange with the solvent, appear as quite broad ragged doublet around 3.46 (ppm) and 3.77 (ppm) coordinated with metals (II) which disappeared in the metal complex spectra. In complex 2 peaks range 1.21-1.76 ppm are from coordinated water. The various assignments of ^1H NMR of the complexes are summarized in table 3. Chemical shift are in ppm from TMS & multiplicity in parentheses (bd, broad; d, doublet; m, multiplet).

Magnetic susceptibility measurements and electronic spectra

The magnetic moment (μ) determined at room temperature is 1.75 BM. This correlates with that of spin-only d^1 electronic configuration of VO^{2+} cation indicating a monomeric complex. The electronic spectrum of the complex is studied in the range of 200-900 nm. Two very strong bands in the region 245-255 and 346-375 nm were observed in the spectrum of the complex, attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the aromatic ring and C=N chromophore [26]. The band 389 nm can either be assigned to $^2\text{B}_2 \rightarrow ^2\text{A}_1$ transition or to the low energy charge transfer /inter ligand transition. In the visible region, the spectrum of the complex shows an absorption band at 675 nm assigned to the $^1\text{B}_2 \rightarrow ^2\text{E}(\text{v})$ in an octahedral configuration in both complexes. The present complex is a six – coordinated complexes having octahedral geometry with oxygen of the vanadyl group at the apex and four atoms of the ligand forming a basal plane.

Kinetics of thermal decomposition

Recently, there has been increasing interest in determining the rate- dependent parameters of solid-state non- isothermal decomposition reactions by analysis of TG curves. Thermogravimetric (TG) and differential thermogravimetric (DTA) analyses were carried out for different metal-streptomycin complexes in ambient conditions. The complexes were decomposed nearly 10% of the total mass up to temperature 175°C , followed by considerable decomposition of the ligand molecule up to 650°C , leaving metal oxide (VO_2) in both complexes as residue. On the basis of thermal

decomposition, the kinetic analysis parameters such as activation energy (E^*), enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), free energy change of decomposition (ΔG^*) were evaluated graphically by employing the Coats – Redfern relation

$$\text{Log} [-\text{Log} (1 - \alpha) / T^2] = \text{log} [AR / \theta E^*(1-2RT/E^*)] - E^*/2.303RT \dots\dots 1$$

Where α is the mass loss up to the temperature T , R is the gas constant, E^* is the activation energy in J mole^{-1} , θ is the linear heating rate and the term $(1-2RT/E^*) \cong 1$. A straight line plot of left hand side of the equation (1) against $1/T$ gives the value of E^* while its intercept corresponds to A (Arrhenius constant). The Coats and Redfern linearization plots, confirms the first order kinetics for the decomposition process. The calculated values of thermodynamic activation parameters for the decomposition steps of the metal complexes are reported in Table 4. According to the kinetic data obtained from the TG curves, the activation energy relates the thermal stability of the metal complexes. All the complexes have negative entropy, which indicates that the complexes are formed spontaneously. The negative value of entropy also indicates a more ordered activated state that may be possible through the chemisorptions of oxygen and other decomposition products. The negative values of the entropies of activation are compensated by the values of the enthalpies of activation, leading to almost the same values for the free energy of activation.

X-ray powder diffraction studies

In absence of single crystal, x-ray powder data is especially useful to deduce accurate cell parameters. The diffraction pattern reveals the crystalline nature of the complex. The indexing procedure were performed using (CCP4, UK) Crysfire programme giving crystal systems cell dimension of the complexes with varying space group. The merit of fitness and particle size of the metal complexes has been calculated from the FWHM (100%) peaks of the complexes.

TOF-MS spectra

Mass spectrometry has been successfully used to investigate molecular species $[MH]^+$ in solution. The molecular ion peaks of the ligands and complexes have been used to confirm the proposed formula. The pattern of the mass spectrum gives an impression of the successive degradation of the target compound. Their intensity gives an idea of stability of fragments. The ligand starts degradation and finally forms $[C_{31}H_{25}NO_7]^+$, 656/657 (100 % m/z values). In the TOF-mass spectra of metal complexes initial fragmentation pattern is again similar, a mononuclear nature for these complexes $[M(L)]^+$ can be deduced. The fragmentation of complexes as m/z : 653.12 (100.0%), 654.12 (34.6%), 655.13 (7.7%), 656.13 (1.4%) of complex 1 and m/z : 790.23 (100.0%), 791.24 (33.5%), 792.24 (8.3%), 791.23 (3.0%), 793.24 (1.7%) of complex 2.

Molecular modeling of complexes

To examine the structural properties, various traditional research techniques were used, but in this article, we were trying to assess observed data at molecular level with the help of molecular modeling. This modeling program was commonly known as computer assisted molecular design (CAMD). Molecular modeling had been successfully used to detect three dimensional arrangements of atoms in MOF. Their utilization in the demonstration of molecular structure of the studied complex was presented in the article. Molecular mechanics was a mathematical formalism, which attempted to reproduce molecular geometries, bond energies and other related features. Bond lengths, bond angles and atomic coordinates and their

values were dependent on the hybridization of an atom and its bonding scheme. So molecular models for V (IV) complexes were obtained by using the commercial available Chem Office Ultra-12 molecular modeling software. These reported statistics have a good correlation with figures 4-5.

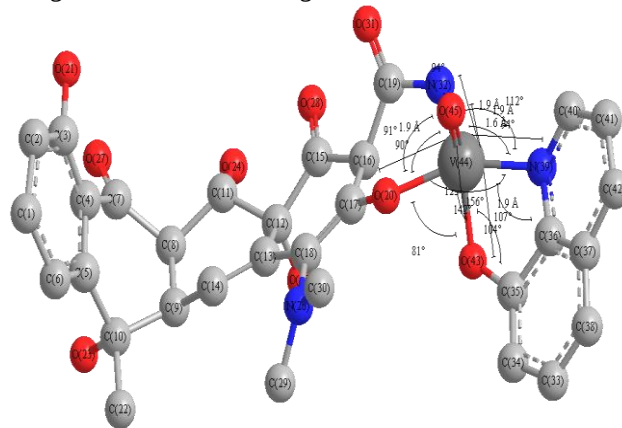


Figure4. Optimised structure of complex 1 with steric energy 88.765 kcal/mol.

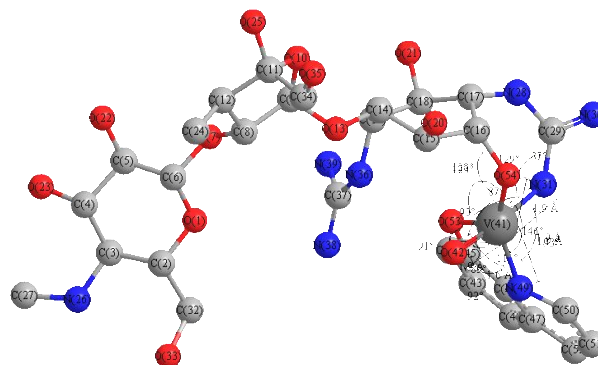


Figure 5. Optimised structure of complex 2 with steric energy 124.3168 kcal/mol.

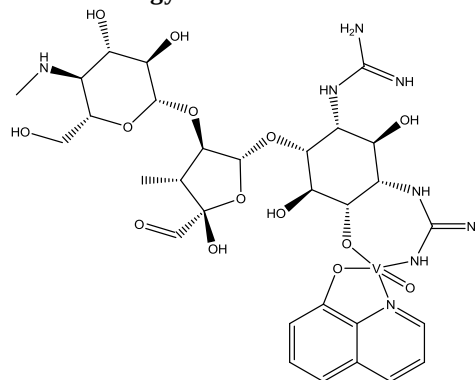


Figure 6. Asymmetry structure of complex2

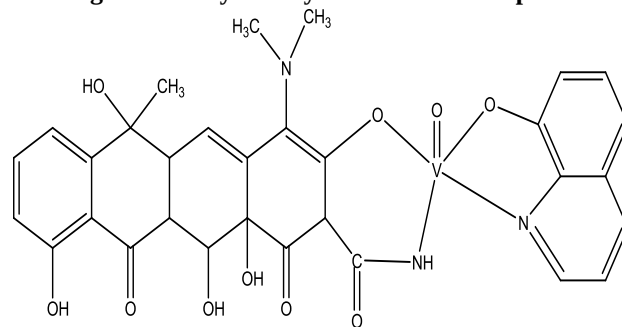


Figure 7. Proposed graphical structure of complex 1.

Table 1. Color, reaction yield and elemental analysis of complexes

Complex	Empirical formula	Color	Yield (%)	Analysis: found (calculated) (%) C H N V	M.Pt. °C
Complex (1)	C ₃₁ H ₂₈ N ₃ O ₁₀ V	blues	80	56.97 4.32 6.43 7.80 (56.98) (4.35) (6.45) (7.81)	55.67
Complex(2)	C ₃₀ H ₄₃ N ₈ O ₁₄ V	white	85	45.57 5.48 14.17 6.44 (45.54) (5.47) (14.18) (6.45)	72.54

Table 2. Assignment of IR spectral data (cm⁻¹) of the metal complexes

Frequency	OH	OH	OH	NH ₂	NH ₂	M – O
C ₃₁ H ₂₈ N ₃ O ₁₀ V	3425(s,b)	1506(s)	1528(s)	1283(m)	660(s)	467(m)
C ₃₀ H ₄₃ N ₈ O ₁₄ V	3429(s,b)	1617(m)	1506(s)	1230(m)	685(s)	425(s)

Table 3. H N M R data of free novel ligands and their complexes

Compounds	Δ (ppm)
Complex1	[3.35(s)1H,OH],16.77(s)1H,OH,1.677(s),1H,OH,3.65(m),5H,OH,2.0(s)1H,NH,7.16(s)1H,NH ₂
Complex2	[8.17(bd)2H,OH],[3.26(m)1H,OH],[1.951(bd)H,NH],[2.05(s)OH],[1.94(d)1H OH]6.54[Ar1H(s)5.04],[4.451H OH],[3.76(m)1H]

Table 4. Thermodynamic activation parameters of the metal complexes

Complex	Order/n	Steps	E*/Jmol ⁻¹	A/sec ⁻¹	ΔS*/JK ⁻¹ mol ⁻¹	ΔH*/Jmol ⁻¹	ΔG*/kJmol ⁻¹	k×10 ⁻² s ⁻¹
Complex 1	1	I	52.66	1.125×10 ⁵	-92.49	112.745	61.228	1.72
		II	63.804	1.256×10 ⁵	-110.175	96.114	89.18	1.02
Complex 2	1	I	53.066	6.27×10 ⁵	-85.136	74.10	55.29	3.27
		II	9.178	1.16×10 ⁵	-109.603	125.89	93.104	1.79

Table5. Crystallographic data of co0mplexes

Compounds	Complex 1	Complex 2
Formula	C ₃₁ H ₂₈ N ₃ O ₁₀ V	C ₃₀ H ₄₃ N ₈ O ₁₄ V
FW	790.23	653.51
Temp (K)	293	293
Wavelength	1.54056	1.54056
Crystal System	Monoclinic	Tetragonal
Space group	P21/M	P4/MM
Unit cell dimension		
a(Å)	14.4988	12.6313
b(Å)	5.95531	12.6313
c(Å)	4.4909	6.3494
α°	90.00	90.00
β°	96.29	90.00
γ°	90.00	90.00
Volume (Å ³)	385.44	1013.06
θ range (0)	21.696-75.106	13.811-61.987
Limiting indices	-9 ≤ h ≤ 0 0 ≤ k ≤ 2 0 ≤ l ≤ 3	1 ≤ h ≤ 6 0 ≤ k ≤ 5 0 ≤ l ≤ 4
Particle size(nm)	17.922	45.82
Intensity (%)	7.2–100	5.9–100
R indices	0.0000156	0.0000615
Density	1.07405	1.7437
Z	2	2
M(20)	14	7
F(20)	5	4
Avs.Eps.	0.0000342	0.0000144

Table6. Selected bond lengths and bond angles of the complexes

Complex 1(C ₃₁ H ₂₈ N ₃ O ₁₀ V)	Complex2 (C ₃₀ H ₄₃ N ₈ O ₁₄ V)
Bond lengths	Bond lengths
N(39)-V(44) 1.9060	O(54)-V(41) 1.8645
O(43)-V(44) 1.8649	N(49)-V(41) 1.9103
N(32)-V(44) 1.8996	O(53)-V(41) 1.8641
O(20)-V(44) 1.8685	N(31)-V(41) 1.9017
V(44)-O(45) 1.6089	V(41)-O(42) 1.6074
V(44)-O(21) 1.6135	V(41)-O(43) 1.7123
Bond angles	Bond angles
N(39)-V(44)-O(43) 81.3283	O(54)-V(41)-N(49)146.4309
N(39)-V(44)-N(32) 112.1179	O(54)-V(41)-O(53)128.2206
N(39)-V(44)-O(20) 156.1292	O(54)-V(41)-N(31)87.1157
N(39)-V(44)-O(45) 94.0865	O(54)-V(41)-O(42)90.1784
O(43)-V(44)-N(32) 122.8599	N(49)-V(41)-O(53)85.2188
O(43)-V(44)-O(20) 81.2430	N(49)-V(41)-N(31) 92.8818
O(43)-V(44)-O(45) 142.1286	N(49)-V(41)-O(42)92.3628
N(32)-V(44)-O(20) 91.0732	O(53)-V(41)-N(31)86.5306
N(32)-V(44)-O(45) 93.8242	O(53)-V(41)-O(42)90.9077
O(20)-V(44)-O(45) 89.7406	N(31)-V(41)-O(42) 173.9517
V(44)-O(43)-C(35) 106.9542	N(32)-V(41)-O(42) 172.876
V(44)-N(39)-C(40) 120.5144	O(54)-V(41)-O(44) 87.547
V(44)-N(39)-C(36) 103.7065	

Conclusions

The complexation behaviour of oxovanadium with mixed ligands containing N,O donor atoms has been synthesized and the most important feature of binding ability of oxovanadium with used ligands good agreement which showed by spectral studied. These atoms formed new bonds with oxovanadium. The binding abilities of the metals were determined by different spectral techniques. To find out the crystal lattice parameters, particle size were calculated and density of the crystal were determined by Archimedes principle. The molecular structures of the complexes were proposed with help of Chem Office Ultra-11 programme. The Metal –organic frame work complexes will be ailment of anti- cancer.

References

1. Y. M. Cui, Y. J. Cai and W. Chen, Synthesis and crystal structures of Schiff base oxovanadium(V) complexes [VO(Bhm)(OCH₃)(CH₃OH)] and [VO₂(Bpp)], Russian Journal of Coordination Chemistry, volume 7, issue 12, pages 908-915 Jan. [2011]
2. Caixia Yuan, Liping Lu, Xiaoli Gao, Yanbo Wu and Maolin Guo, Ternary oxovanadium(IV) complexes of ONO-donor Schiff base and polypyridyl derivatives as protein tyrosine phosphatase inhibitors: synthesis, characterization, and biological activities, Journal of Biological Inorganic Chemistry, 4, 6, 841-851 Sep. [2009]
3. Beatriz S. Parajón-Costa, Enrique J. Baran, Vibrational spectra oxovanadium(IV): A potent insulin mimetic agent Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 78, Issue 1, Pages 133-135 January 2011.
4. M.L. Sharma, S.K. Sengupta, O.P. Pandey, Template synthesis, spectroscopic characterization and preliminary insulin-mimetic activity of oxovanadium(IV) complexes with N₂O₂ diazadiox macrocycles, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 95, Pages 562-568, September 2012,
5. B.T. Thaker, R.S. Barvalia, Ligating behaviour of Schiff base ligands derived from heterocyclic β-diketone and ethanol or propanol amine with oxovanadium (IV) metal ion, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 74, Issue 5, Pages 1016-1024, December 2009,
6. F.Y. Bai, X.T. Li, G.S. Zhu, Y.H. Xing Synthesis and structure of a new scorpionate-dithio carboxyl oxovanadium complex and an organic dithio carboxyl compound, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 75, Issue 5, Pages 1388-1393, May 2010.
7. A.Z. El-Sonbati, A.A.M. Belal, M.S. El-Gharib, Sh.M. Morgan Supramolecular structure, mixed ligands and substituents effect on the spectral studies of oxovanadium(IV) complexes of bioinorganic and medicinal relevance Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 95, Pages 627-636, September 2012,
8. Maria Rangel, M. João Amorim, Ana Nunes, Andreia Leite, Eulália Pereira, Baltazar de Castro, Carla Sousa, Yutaka Yoshikawa, Hiromu Sakurai, Novel 3-hydroxy-4-pyridinonato oxovanadium(IV) complexes to investigate structure/activity relationships, Journal of Inorganic Biochemistry, Volume 103, Issue 4, Pages 496-502, April 2009,
9. R. Garg, N. Fahmi and R. V. Singh, Synthetic, spectral, and antimicrobial aspects of biologically relevant coordination compounds of dioxomolybdenum(VI) and oxovanadium(V), Russian Journal of Coordination Chemistry, Volume 34, Number 3, Pages 198-203, [2008].
10. Ana M. Metelo, Rocio Pérez-Carro, M. Margarida C.A. Castro, Pilar López-Larrubia VO(dmpp)₂ normalizes pre-diabetic parameters as assessed by *in vivo* Magnetic Resonance Imaging and Spectroscopy, Journal of Inorganic Biochemistry, In Press, Accepted Manuscript, Available online 13 June 2012
11. Katherine H. Thompson, Jay Lichter, Carl LeBel, Michael C. Scaife, John H. McNeill, Chris Orvig, Vanadium treatment of type 2 diabetes: A view to the future, Journal of Inorganic Biochemistry, Volume 103, Issue 4, Pages 554-558, April 2009,
12. Ming-jin Xie, Xiao-Da Yang, Wei-ping Liu, Shi-ping Yan, Zhao-hui Meng, Insulin-enhancing activity of a dinuclear vanadium complex: 5-chloro-salicylaldehyde ethylenediamine oxovanadium(V) and its permeability and cytotoxicity Journal of Inorganic Biochemistry, Volume 104, Issue 8, Pages 851-857, August 2010,
13. Ming Li, Wenjun Ding, Bharat Baruah, Debbie C Crans, Ruilin Wang, Inhibition of protein tyrosine phosphatase 1B and alkaline phosphatase by bis(maltolato)oxovanadium(IV), Journal of Inorganic Biochemistry, Volume 102, Issue 10, Pages 1846-1853, October 2008.
14. Susana B. Etcheverry, Daniel A. Barrio, Juan Zinczuk, Patricia A.M. Williams, Enrique J. Baran, Synthesis, characterization and biological activity of oxovanadium (IV) complexes with cyclic polyalcohols, Journal of Inorganic Biochemistry, Volume 99, Issue 12, Pages 2322-2327, December 2005.
15. Parashuram Mishra and Bibhesh K. Singh et al. synthesis, characterization and XRPD studies of bioactive complex of oxovanadium, J. coordination Chemistry, Vol. 60, No. 20 pages 2243-2255, October 2007.
16. P.B. Sreeja, M.R. Prathapachandra Kurup, Synthesis and spectral characterization of ternary complexes of oxovanadium(IV) containing some acid hydrazones and 2,2'-bipyridine, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 61, Issues 1-2, 1 Pages 331-336, January 2005,
17. Veli T. Kasumov, F. Köksal, M. Aslanoglu, Y. Yerli, Synthesis, spectroscopic characterization and reactivity studies of oxovanadium(IV) complexes with bulky N,N'-polymethylenebis(3,5-^tBu₂salicylaldehyde) ligands, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 77, Issue 3, 15 Pages 630-637, October 2010.
18. A.Z. El-Sonbati, A.A.M. Belal, M.A. Diab, M.Z. Balboula, Polymer complexes. LVIII. Structures of supramolecular assemblies of vanadium with chelating groups, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 78, Issue 3, Pages 1119-1125, March 2011.
19. Balram Prasad Baranwal, Kiran Tripathi, Alok Kumar Singh, Saurabh Tripathi Synthesis and spectral characterization of ternary mixed-vanadyl β-diketonate complexes with Schiff bases, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 91, Pages 365-369, June 2012.
20. Neema Ani Mangalam, M.R. Prathapachandra Kurup, Synthesis and spectral investigations of vanadium(IV/V) complexes derived from an ONS donor thiosemicarbazone ligand, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 71, Issue 5, Pages 2040-2044, January 2009,
21. Azza A.A. Abou-Hussein, Wolfgang Linert, Synthesis, spectroscopic and biological activities studies of acyclic and macrocyclic mono and binuclear metal complexes containing a hard-soft Schiff base, Spectrochimica Acta Part A: Molecular

and Biomolecular Spectroscopy, Volume 95, Pages 596-609, September 2012.

22. B. Singh and A. K. Srivastav, Synthesis and structural studies of 2-acetylthiophene-2-thenoylhydrazone complexes of oxovanadium(IV), manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II), Journal of Chemical Sciences, Volume 104, Number 4, Pages 457-469, June 2012.

23. Bhavna J. Pandya and Pabitra K. Bhattacharya, Binary and ternary complexes of oxovanadium(IV) and homobinuclear double-bridged oxovanadium(IV) complexes Transition Metal Chemistry, Volume 12, Number 5, Pages 398-400, Feb. 2012.

24. Maria Rangel, M. João Amorim, Ana Nunes, Andreia Leite, Eulália Pereira, Baltazar de Castro, Carla Sousa, Yutaka

Yoshikawa, Hiromu Sakurai, Novel 3-hydroxy-4-pyridinonato oxidovanadium(IV) complexes to investigate structure/activity relationships, Journal of Inorganic Biochemistry, Volume 103, Issue 4, Pages 495-501, April 2010.

25. Katherine H. Thompson, Chris Orvig, Vanadium in diabetes: 100 years from Phase 0 to Phase I, Journal of Inorganic Biochemistry, Volume 100, Issue 12, Pages 1925-1935, December 2006.

26. Mario Gabričević, Erim Bešić, Mladen Biruš, Achim Zahl, Rudi van Eldik, Oxidation of hydroxyurea with oxovanadium(V) ions in acidic aqueous solution, Journal of Inorganic Biochemistry, Volume 100, Issue 10, Pages 1606-1613, October 2006,