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Molybdenum, Nickel, Titanium and Vanadium Complexes of Triethylene Tetramine, Diethylene Triamine Based Schiff Bases

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Schiff base complexes of Mo(VI), Ni(II), Ti(IV) and V(V) formed from salicylaldehyde and triethylenetetramine (trien) namely $(Ni^{2+}L_1).2H_2O$, $[Ti^{4+}(L_1H_2)(C_2O_4)_2].2H_2O$, $[V^{5+}O_2L_1H]\cdot 2H_2O$ and $[Mo^{6+}O_2[L_1H_2)]$ $Mo^{6+}O_4$ where L_1H_2 represents the trien Schiff base and Mo(V), Ni(II), Ti(III) and V(V) complexes formed from salicylaldehyde and diethylenetriamine (dien) namely $[Ni^{2+}(L_2H)_2].H_2O$, $[KTi^{3+}(L_2H)_2C_2O_4]$, $[V^{5+}O_2(L_2H)]$ and $[Mo^{5+}L_2]_2$ $(Mo^{6+}O_4)_3.2H_2O$ where L_2H_2 represents the dien Schiff base are reported. The complexes have been characterized by elemental and thermal analysis, conductivity studies, IR, NMR, EPR and UV-VIS studies. Some of the complexes show promising antibacterial activity against bacterial *K. pneamonia*, *E. coli*, *P. vulgaris*, *Salmonella typhi*, *E. faecalis*, *P. aeruginosa*, *S. epidermis*, methiciline resistant *S. aureus*, ciprofloxin resistant *E. coli* and carbapennen resistant *A. baumanii*.

Key Words: Trien salicylaldehyde Schiff bases-dien salicylaldehyde Schiff bases, Antibacterial studies, Titanium, Vanadium, Nickel, Molybdenum.

INTRODUCTION

Schiff base complexes have a variety of applications in biological, clinical, analytical and pharmacological areas[1-3]. Studies of a new kind of chemotherapeutic Schiff bases are now attracting the attention of several chemists[4,5]. Earlier work reported that some drugs showed increased activity, when administered as metal complexes rather than as organic compounds[6,7]. In this paper, we report the synthesis, characterization and antibacterial studies of complexes of nickel, titanium, vanadium and molybdenum with Schiff bases derived from triethylenetetramine/diethylenetriamine and salicylaldehyde.

EXPERIMENTAL

All reagents and solvents used were of analytical grade and used without further purification. The metal salts used for the preparations are nickel chloride, potassium titanium(III) oxalate, ammonium metavanadate and ammonium molybdate. The analysis of metals is done by Perkin-Elmer Optima 5300 DV induced coupled plasma -optical emission spectrometer and nitrogen analysis by Kjeldahl's method. Thermogravimetry and differential thermal analysis of the complexes were carried out on a recording NETZSCH STA 409C/CD thermal analyzer in nitrogen atmosphere at a rate of 10 ºC/min in platinum crucible. Magnetic measurements were made at room temperature using vibrating magnetometer EG & GPARC model: 155. The UV-visible spectra were recorded on a varian cary spectrophotometer 5E UV-NIS-NIR using mull technique for insoluble complexes and as solutions in DMSO for soluble complexes. IR spectra of the complexes were recorded on a Bruker, IFS 66V FT-IR spectrometer in 4000-400 cm^{-1} range using KBr pellet. ^1H NMR spectra (400 MHz) of the DMSO soluble diamagnetic complexes were recorded in DMSO-d_6 by employing TMS as internal standard using JEOL MODEL:GSX.

Electron paramagnetic resonance spectra of the paramagnetic complexes were recorded using varian E-112 electron spin resonance spectrometer in the region from 1000-8000 gauss at operating frequency 930 GHz. The elemental analysis of the complexes were done using ICP-OES Perkin-Elmer optima 5300 DV 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 method[8].

Synthesis of trien Schiff base complexes: 0.01 mol of triethylene tetramine (trien) and 0.02 mol of salicylaldehyde were mixed simultaneously. To that added 0.01 mol of metal solution. Little amount of alcohol was also added. The solid complex obtained was filtered and dried. Refluxing is done for 2 h only for Ni complex to obtain the solid complex.

Synthesis of dien Schiff base complexes: 0.02 mol of diethylene tetramine (dien) and 0.04 mol of salicylaldehyde were mixed simultaneously. Yellow coloured Schiff base obtained was dissolved in alcohol. 0.01 mol of metal solution was added to the above solution. The solid complex obtained was filtered and dried. In addition 0.04 mol of KOH was added to obtain nickel and vanadium complexes.

RESULTS AND DISCUSSION

The elemental analysis (Table-1) on the complexes indicate the following compositions where L_1H_2 and L_2H_2 represent the Schiff bases formed from trien and dien, respectively.

$[Ni^{2+}L_1].2H_2O$	$[Ni^{2+}(L_2H)_2].H_2O$
$[Ti^{4+}(L_1H_2)(C_2O_4)_2].2H_2O$	$[KTi^{3+}(L_2H)_2C_2O_4]$
$[V^{5+}O_2(L_1H)].2H_2O$	$[V^{5+}O_2(L_2H)]$
$[Mo^{6+}O_2(L_1H_2)]MoO_4$	$[Mo^{5+}L_2]_2(MoO_4)_3.2H_2O$

The Ni and Ti dien complexes were soluble in both DMSO and $CHCl_3$ while Ti trien complex is soluble only in DMSO. Mo trien complex is soluble in DMSO whereas Mo dien and vanadium complexes were insoluble in most of the solvents.

The TGA and DTA data on the complexes are given in Table-2. First stage corresponds to loss of water and the final stage corresponds to metal oxide formation.

TABLE-1
PHYSICAL CHARACTERIZATION, ANALYTICAL, CONDUCTIVITY, MAGNETIC AND UV-VISIBLE SPECTRAL DATA ON COMPLEXES

Complexes	Colour	Magnetic Data	Molar conductance (ohm^{-1} cm^2/mol)	Found (Calculated) %			λ_{max} nm
				M	N	MO	
$[Ni^{2+}L_1].2H_2O$	Brown	Diamagnetic	15	13.5 (13.02)	11.82 (12.57)	16.2 (16.59)	370
$[Ti^{4+}(L_1H_2)(C_2O_4)_2].2H_2O$	Yellow	Diamagnetic	14	7.82 (8.6)	8.97 (9.4)	14.9 (14.1)	Below 300
$[V^{5+}O_2(L_1H)].2H_2O$	Yellow	Diamagnetic	-	10.12 (10.80)	10.97 (11.86)	18.07 (19.27)	311, 393
$[Mo^{6+}O_2(L_1H_2)].MoO_4$	Pale green	Diamagnetic	78	29.52 (29.90)	7.95 (8.72)	45.02 (44.85)	255, 310
$[Ni^{2+}(L_2H)_2]H_2O$	Reddish brown	Diamagnetic	14	9.02 (8.33)	12.09 (12.06)	-	389, 314
$[Kti^{3+}(L_2H)_2C_2O_4]$	Yellow	Paramagnetic	21	Ti 5.86 (6.03) K 4.08 (4.90)	11.95 (10.56)	16.8 (15.97)	320
$[V^{5+}O_2\ (L_2H)]$	Yellow	Diamagnetic	-	13.31 (12.97)	10.98 (10.68)	23.75 (23.15)	322
$[Mo^{5+}L_2]_2(Mo^{VI}O_4)_3.2H_2O$	Pale green	Paramagnetic	-	36.71 (36.19)	7.05 (6.33)	55.0 (54.29)	273, 325

TABLE-2
TGA AND DTA DATA ON THE COMPLEXES ENDOTHERM (-) EXOTHERM (+)

Complexes	Loss of water		Formation of metal oxide		DTA data
	Temp. (ºC)	Water loss (%)	Temp. (ºC)	Water loss (%)	
$[Ni^{2+}L_1].2H_2O$	No distinct peak	-	150-1200	16.20 (16.59)	55(-), 143 (+) 274 (+)
$[Ti^{4+}(L_1H_2)(C_2O_4)_2].2H_2O$	6.8 (5.52)	50-120	150-800	15.02 (14.1)	58 (-), 226 (-) 513.2 (-)
$[V^{5+}O_2(L_1H)].2H_2O$	No distinct peak	-	150-1000	18.07 (19.27)	89.5(-), 250(-), 1086.9(-)
$[Mo^{6+}O_2(L_1H_2)].MoO_4$	-	-	150-900	45.02 (44.85)	214.7(+), 327.7 (+) 620 (-)
$[Ni^{2+}(L_2H)_2].H_2O$	2.4 (2.5)	50- 90	150-1200	-	85.7 (-) 165.7 (+) 611.1 (+)
$[Kti^{3+}(L_2H)_2C_2O_4]$	-	-	160-1100	14.80 (15.97)	103 (+), 603.9 (-), 1056.1 (+)
$[V^{5+}O_2(L_2H)]$	-	-	150-1400	23.75 (23.15)	96 (+), 200 (+) 417.9 (+), 602 (-)
$[Mo^{V}L_2]_2(Mo^{VI}O_4)_3.2H_2O$	2.2 (2.7)	50-120	150-950	55.00 (54.29)	64.28 (-), 85.8 (+) 190.2 (+), 331.3 (+)

Magnetic susceptibility of the complexes indicate all trien complexes are diamagnetic confirming with Ni(II) square planar. The dien complexes with V and Ni are diamagnetic confirming vanadium is in +5 oxidation state and Ni(II) is in square planar arrangement whereas Ti and Mo dien complexes are paramagnetic corresponding to the presence of one and two electrons/complex molecule, respectively which corresponds to Ti in +3 state and Mo in +5 state, respectively. The nickel dien and trien complexes showed absorptions at 389, 314 and 370 nm, respectively corresponding to *d*→*d* transition. V(V) dien and trien complexes showed peaks at 322, 311 and 393 nm, respectively. The bands in the region 310-325 nm may be due to O→V(V) charge transfer. The band at 393 nm in trien complex may be due to Schiff base to V(V) charge transfer. Schiff base to metal charge transfer is high energetic and goes below 300 nm in Ti trien complex. In Mo dien complex, *d*→*d* transition appears at 325 nm while O→Mo charge transfer appears at 273 nm. Ti(III) dien complex showed a band at 320 nm due to *d*→*d* transition. In Mo trien complex, MoO_4^{2-} charge transfer appears at 255 nm and band at 310 nm may be due to Schiff base to Mo(VI) charge transfer.

IR spectra of the complexes show strong bands in the region around 1630 cm^{-1} and may be assigned to ν(C=N) of Schiff base. The Ti complex alone showed a characteristic band at 1695 cm^{-1} confirming the presence of coordinated oxalato group. The ν(V=O) of vanadium complexes appears at 896 and 940 cm^{-1} for trien and dien complexes respectively. ν(Mo=O) of the Mo trien complex appears at 931 and 889 cm^{-1} corresponding to molybdenyl cation and molybdate anion, respectively ν(Mo=O) of Mo dien complex appears at 886 cm^{-1} for MoO_4^{2-} ion and no distinct peak appears at 930 cm^{-1} indicating the absence of molybdenyl cation.

In the NMR spectra of Mo trien and Ni dien complexes (Table-3), CH_2 protons appears around the region 2-4. The aromatic protons appear in the region 6.0-7.5 as multiplet due to *ortho* substitution and protons of the imine group appears at 7.4 ppm. The -NH protons of the secondary amino group appears in the region 8.0-8.5. The hydrogen bonded -OH protons of the salicylaldehyde group appears around 13.0-13.5 ppm.

TABLE-3
NMR SPECTRAL DATA ON COMPLEXES

$[Mo^{6+}O_2(L_1H_2)].MoO_4$	$[Ni^{2+}(L_2H)_2].H_2O$	Assignments
2.7 (t), 3.6 (t)	3.5 (t)	Dien/trien moiety
6.8 – 7.3 (m)	6.5 – 7.3 (m)	Aromatic
7.4 (s)	7.4 (s)	-CH (imine group)
8.3 (s)	8.4 (s)	- NH
13.2 (s)	13.3 (s)	Hydrogen bonded - OH

In the EPR spectrum of Mo dien complex single peak appears in the region 3384.6 gauss. Which corresponds to g value of 1.98. For titanium complex three peaks appear in the region 1678.6, 2535.7, 3356.8 gauss corresponding to g values of 3.8, 2.6 and 2.03, respectively. Perhaps g value of 3.8 corresponds to $g_{\perp}$ and 2.03 corresponds to $g_{\parallel}$ and g value of 2.6 corresponds to average value. A very high g value may be indicative of extreme anisotropic arrangement of titanium.

The trien complexes of Ni, Ti and Mo were tested against various bacteria. 1.25-5.00 mg of samples have been tried for anti-bacterial test. As the concentration increases activity also increases. The inhibitory diameter zone for the complexes as against the standard are summarized in Table-4. The standard used was streptomycin. It is promising that the complexes are active against a range of bacteria especially methiciline resistant *S. aureus* (MRSA), ciprofloxin resistant *E. coli* (CRE) and carbapennen resistant *A. baumanii* (CRA) against which standard streptomycin is inactive.

TABLE-4
ANTIBACTERIAL ACTIVITY OF METAL COMPLEXES

Complex	mg/disc	Disc diffusion method-diameter of inhibitory zone (mm)									
		KP	EC	PV	ST	EF	PA	SE	MRSA	CRE	CRA
$[Ni^{2+}L_1].2H_2O$	1.25	-	-	-	-	-	8	-	-	8	-
	2.50	9	9	12	-	8	8	-	9	8	9
	5.00	11	12	14	11	11	12	-	12	10	12
$[Ti^{4+}(L_1H_2)(C_2O_4)_2].2H_2O$	1.25	8	9	-	-	-	8	8	-	8	8
	2.50	11	11	-	-	8	8	10	10	9	10
	5.00	14	14	-	12	9	10	13	14	12	12
$[Mo^{6+}O_2(L_1H_2)].MoO_4$	1.25	8	8	10	-	8	8	9	8	10	8
	2.50	11	11	13	10	11	12	12	11	12	12
	5.00	15	15	15	12	17	13	15	-	-	-
Streptomycin	30 µg/disc	15	15	15	12	17	13	15	-	-	-

KP = *K. pneamonia*, EC = *E. coli*, PV = *P. vulgaris*, ST = *Salmonella typhi*, EF = *E. faecalis*, PA = *P. aeruginosa*, SE = *S. epidermis*, MRSA = Methiciline resistant *S. aureus*, CRE = Ciprofloxin resistant *E. coli*, CRA = Carbapennen resistant *A. baumanii*

Based on the above discussions nickel(II) and Ti(III) dien Schiff base complexes contain two schiffbase units/complex molecule. Ni(II) forms a square planar arrangement with four imine nitrogen coordination. Two OH groups of the salicylaldimino group are deprotonated and the O involve in hydrogen bonding with OH group of adjacent salicylaldimino groups. Four imine nitrogens and an oxalato group octahedrally surround Ti^{3+}. One OH of each Schiff base unit remains deprotonated, one of which remains as an ion pair with K^+ while other O involves in hydrogen bonding with OH of adjacent salicylaldimino groups. There can perhaps be hydrogen bonding interaction between OH group of salicylaldimino group and oxalato oxygen.

In the complex with vanadium(V), VO_2^+ is surrounded by one dien Schiff base with two imine nitrogens and two oxygen atoms of salicylaldimino group where one of the OH is deprotonated. Mo(V) is perhaps five coordinate with two imine nitrogens and one NH nitrogen and two oxygens of deprotonated OH of salicylaldimino group.

The Mo(V) complex species carries 3+ charges and is balanced with molybdate counter ions. In the trien complexes as Ni(II) is diamagnetic, a square planar arrangement with two imine nitrogens and two O of deprotenated OH of salicylaldimino groups is proposed. The VO^{2+} and MoO_2^{2+} are surrounded by two NH nitrogen atoms of trien and two imine nitrogen atoms. The molybdenum complex contains MoO_4^{2-} counter anion. One of the OH of salicylaldimino group is deprotonated and perhaps involves in hydrogen bonding with the other OH group in the vanadium complex. Titanium(IV) complex may be eight coordinate with two oxalato ligands and two N-H nitrogens and two imino nitrogens surrounding the metal.

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REFERENCES

1. T. Hitoshi, N. Tamao, A. Hideyaki, F. Manabu and M. Takayuki, *Polyhedron*, **16**, 3787 (1997).
2. T. Punniyamurthy, S.J.S. Kalra and J. Iqbal, *Tetrahedron Lett.*, **36**, 8497 (1995).
3. G.S. Trivedi and N.C. Desai, *Indian J. Chem.*, **31B**, 366 (1992).
4. Y.K. Choi, K.H. Chjo, S.M. Park and N. Doddaponani, *J. Electrochem. Soc.*, **142**, 4107 (1995).
5. B. Katia, L. Simon, R. Anne, C. Gerard, D. Francoise and M. Bernard, *Inorg. Chem.*, **35**, 387 (1996).
6. E.M. Hodnett and P.D. Mooney, *J. Med. Chem.*, **13**, 786 (1970).
7. E.M. Hodnett and W.J. Dunn, *J. Med. Chem.*, **15**, 339 (1972).
8. Biological Evaluation of Plants with Reference to the Malagasy Flora, Monograph for the IFS-NAPRECA Workshop on Broadssays, Antananarivo, Madagascar, pp. 72-79.

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