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SYNTHESIS AND CHARACTERIZATION OF SOME VANADYL SCHIFF BASES COMPLEXES.

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ABSTRACT

Neutral tetradentate N2O2 type complexes of vanadium(IV) have been synthesized using a Schiff base formed by the condensation of o-aminobenzoicacid, o-aminophenol. Benzidin and 1,4-phenylenediamine with Benzil, saliasldehyde, and 2-methlycyclo-pentane-1,3-dione in alcohol medium. All the complexes were characterized on the basis of their micro analytical data, elemental analysis, melting points, IR, UV–Vis spectra and magnetic moment properties. The infrared spectrum of the complexes under investigation confirmed the site of chelation, hence, the complexes showed strong absorptions due to ν(C=N) and ν(C—O). The above absorptions have been shifted on complexation confirming the chelation positions. The UV–Vis spectral data and the magnetic moment suggested that all the complexes are square pyramidal geometry. The vanadyl(IV) complexes showed the mononuclear and polynuclear metal structures. Due to the complexity of the vanadyl complexes under investigation further study are in progress.

Keywords: Benzidin, saliasldehyde, square pyramidal and vanadyl complexes.

INTRODUCTION

The complexes of transition metals have been used in solution as biomimetic catalysts for oxygen atom transfer, and as catalysts for enantioselective epoxidation, aziridinations, mediating organic redox reactions and other oxidative processes. Vanadium is a physiologically important trace element that is found in both anionic and cationic forms with oxidation states ranging from -1 to +5.[1-3] Vanadyl(IV) complexes are very interesting as model compounds for the clarification of several biochemical processes.[24] The physico-chemical properties of vanadyl(IV) complexes have been used to treat both insulin-dependent type-1 and non-insulin-dependent type-2, the vanadyl(IV) complexes proposed on the basis of the results of diabetic model animals by using a concept of equivalent transformation, which proven to be effective in changing the chemical property of a complex.[5] The Vanadyl and the micro-mineral derived from Vanadium, has been shown effective in helping to increase Insulin sensitivity.The main advantages of increased Insulin sensitivity are that it could promote less fat storage as well as that it may act as an Amino Acid magnet to cells. Several pharmaceutical agents have been used in diabetes treatment but many problems occurred such as side effect, hypoglycemia and weight gain, therefore new drug are needed, the vanadyl complexes have been proposed to function as potent insulin-mimetic and antidiabetic agents.[6]

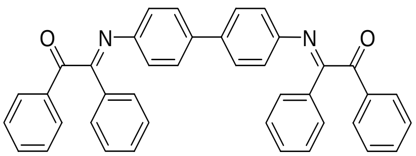
EXPERIMENTAL

The materials and reagents used in this study were laboratory pure chemical. They include, Benzil, saliasldehyde, 2-methlycyclopentane-1, 3-dione, 1.4-phenylenediamine, Benzidin, o-aminobenzoicacid and o-amino phenol. The solvent used are ethanol, acetone, dimethylformamide (DMF), chloroform ($CHCl_3$), distilled water and diethyl ether (40 -60C°). The metal used is Ammonium-Meta-vanadate [NH_4VO_3].

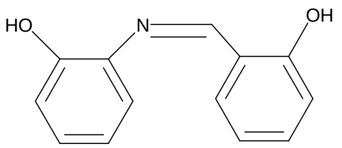
Synthesis of the Schiff base ligand

An ethanolic solution (20ml) of amine was refluxed with ketone or aldehyade for about 12hrs. The reaction molar ratio was 1:2 or 1:1 (amine to ketone or aldehyade). The volume of the solution was reduced to one third, and then it was added with consonant stirring. The result which formed was filtered, washed, recrystallized from ethanol and dried in vacuum. This method was based on the previous methods reported for the preparation Schiff base ligands.

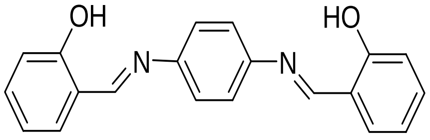
The ligand $C_{40}H_{28}N_2O_2$ prepared from the reaction of benzidin with benzyl, the ligand $C_{13}H_{11}NO_2$ prepared from the reaction of o-aminophenol with saliasldehyde, the ligand $C_{20}H_{16}N_2O_2$ prepared from the reaction of p-aminoaniline with saliasldehyde and finally the ligand $C_{20}H_{18}N_2O_4$ prepared from the reaction of o-aminobenzoicacid with 2-methylcyclopentane-1,3-dione. The ligands structure as follows:



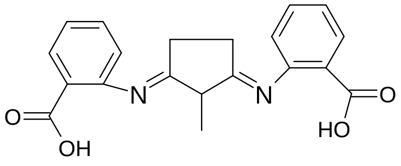
$C_{40}H_{28}N_2O_2$



$C_{13}H_{11}NO_2$



$C_{20}H_{16}N_2O_2$



$C_{20}H_{18}N_2O_4$

Synthesis of Synthesis of the Schiff base complexes

Schiff base complexes under investigation were synthesized as follows; the ligand was dissolved in (20 cm^3) ethanol and added to a metal chloride salts ethanolic solution (20 cm^3).

The reaction molar ratio is (1:1) or (1L: 2M). The mixture was refluxed for 10h; the volume of the mixture was reduced to one-third. On cooling a crude product was formed, which is collected by filtration and washed several times with ethanol and dried over anhydrous $CaCl_2$.

Measurements

The Schiff base ligand and its complexes under investigation were subjected to (C, H and N) elemental analysis which performed at analytic unit of the central laboratory of RASCO Company Libya. The melting points were measured in capillary tubes Philip Harris, Shenston-England, serial NO.B/A_211. The molar conductance values were calculated in (10^{-3}M) in DMF or Chloroform solution by using digital conductivity meter CMD 650. The magnetic moment measurements were determined by using a modified Goy type magnetic balance Hertz SG8 SHJ, England. The electronic absorption spectrum was carried out by using a Perkin –Elmer Lambda 4β spectrophotometer in 1cm matched silica cells using $CHCl_3$ as a solvent.

RESULTS AND DISCUSSION

The Schiff base ligands under investigation were formed by the condensation reaction of benzidin with benzyl, o-aminophenol with saliasldehyde, p-aminoaniline with saliasldehyde and o-aminobenzoicacid with 2-methylcyclopentane-1,3-dione to obtained $C_{40}H_{28}N_2O_2$, $C_{13}H_{11}NO_2$, $C_{20}H_{16}N_2O_2$ and $C_{20}H_{18}N_2O_4$ respectively.

Elemental analysis

The elemental analysis of C, H and N of the compounds considered are listed in Table 1. The results of C, H and N percentage are in agreement with the composition suggested for the ligand and the vanadyl complexes.

Table-1: Elemental analysis, color and melting points of Schiff bases and their vanadyl complexes.

Complex	$M.w_t$	color	m.p C°	Found (calc.)		
				C%	H%	N%
$C_{40}H_{28}N_2O_2.2H_2O$	605.67	Olive green	230C°	78.79 (79.45)	4.98 (5.33)	5.31 (4.63)
$C_{13}H_{11}NO_2$	213.23	bright red	185C°	72.64 (73.22)	5.34 (5.19)	6.64 (6.56)
$C_{20}H_{16}N_2O_2$	316.35	orange	208C°	74.91 (75.93)	5.19 (5.09)	8.94 (8.85)
$C_{20}H_{18}N_2O_4$	350.38	Yellow	240C°	68.36 (68.56)	6.00 (5.18)	7.90 (8.00)
$C_{80}H_{56}N_4O_6V_2$ .5H_2O	1361.28	Pale Green	>250	70.03 (70.58)	4.62 (4.89)	5.35 (4.12)
$C_{26}H_{20}N_2O_5V.2H_2O$	527.42	Brown	>250	58.35 (59.21)	3.66 (4.59)	6.22 (5.31)
$C_{40}H_{28}N_4O_6V_2$ .2H_2O	798.59	Dark Brown	>250	60.15 (60.16)	4.01 (4.04)	7.01 (7.02)
$C_{20}H_{18}N_2O_5V.3H_2O$	471.35	Pale Green	>250	50.66 (50.96)	4.69 (5.13)	7.10 (5.94)

Infrared spectra of the ligands

The infrared spectra data is shown in Table 2, the assignment of infrared bands of the Schiff basees and their vanaday complexes are in agreement with the expected values. The ligands showed the following bands, a band in the range of 3363-3396 cm^{-1} is attributed to the OH group. A band at 1588-1662 cm^{-1} is due to ν(C=N) vibration. Meanwhile, the band at 1720-1730 cm^{-1} is assigned to ν(C=O) stretching frequency. The C—O stretching absorption is seen at range 1211-1366 cm^{-1}. For instance, the IR spectrum of Schiff base ligand derived from Benzidin and benzil $C_{40}H_{28}N_2O_2$ Showed medium broad band at 3377 cm^{-1}, which may be due to ν (OH), The intense band at 1286cm^{-1}, present in IR spectrum of the Schiff base assigned to ν(C—O) stretching mode, The band at 1619 cm^{-1}, can be very safely assigned to ν (C=N) azomethine group stretching. Also a weak medium band at 1730cm^{-1} which the ν (C=O) group.

Infrared spectra of the complexes

The IR spectra of the complexes compared with those of the ligand indicate that the ν(C=N) band at (1594 to 1622 cm^{-1}) which are shifted on complexation. The IR spectra showed a band at (1234 to 1292 cm^{-1}) attributed for ν(C—O) stretching. The OH stretching for the complexes are appeared on the region at (3225 to 3418 cm^{-1}). The ν(C=O) stretching absorption are emerged at the region (1720 to 1738 cm^{-1}). Conclusive evidence of bonding is also shown by the observation of new bands in the spectra of the metal complexes appear at (951 to 986 cm^{-1}) and (428 to 490 cm^{-1}) these are assigned to ν(V—O) and ν(V—N) stretching respectively, these two bands are not observed in the spectra of the ligands. Our IR results are similar to those observed previously.[7]

The electronic spectra of Schiff base ligands

The Uv-vis spectra of the ligands and their vanadyl complexes are listed in Table 3. The electronic spectra are measured in 10^{-3}M DMF or Chloroform. The ligand spectra showed the expected $\pi \rightarrow \pi *$ transition at the region (38022-49571cm^{-1}).

Table-2 : Infrared bands assignments (cm^{-1}) of the Schiff bases and their vanadyl complexes.

The complex	ν(C=N) cm^{-1}	ν(C =O) cm^{-1}	ν(OH) cm^{-1}	ν(C–O) cm^{-1}	ν(V-O) cm^{-1}	ν(V-N) cm^{-1}
$C_{40}H_{28}N_2O_2.2H_2O$	1619	1730	3377	1286	-	-
$C_{13}H_{11}NO_2$	1631	-	3380	1274	-	-
$C_{20}H_{16}N_2O_2$	1609	-	3396	1280	-	-
$C_{20}H_{18}N_2O_4$	1588	1720	3363	1285	-	-
$C_{80}H_{56}N_4O_6V_2\ .5H_2O$	1622	1730	3225	1289	980	490
$C_{26}H_{20}N_2O_5V.2H_2O$	1606	-	3404	1234	962	475
$C_{40}H_{28}N_4O_6V_2\ .2H_2O$	1612	-	3238	1283	951	485
$C_{20}H_{16}N_2O_5V\ .3H_2O$	1594	1738	3418	1292	986	428

The electronic spectra and magnetic measurements of the complexes

The magnetic moment values, $\mu_{eff,}$ measured for all complexes at room temperature (298 K) and recorded in the solid state are given in Table 3. The vanadyl complexes showed comparable values for Magnetic and electronic measurements. The electronic spectra of the vanadyl complex $C_{80}H_{56}N_4O_6V_2\ .5H_2O$ exhibits bands at 11834 cm^{-1}and 22471 cm^{-1} which can be assigned to the $^2B_2 \rightarrow {}^1A_1$ and $^2B_{2(P)} \rightarrow E$ transition and the band at 27173 cm^{-1} is assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic ring or azomethine group which agreeable with the reported results. These transition, as well as the measured value of magnetic moment (1.2 B.M) suggest square pyramidal stereochemistry of the complex.. These results are in excellent agreement with those achieved earlier.[8]

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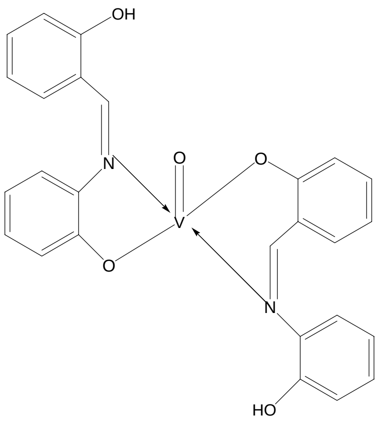
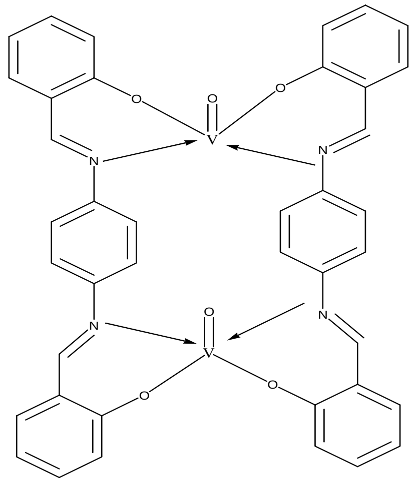


$C_{26}H_{20}N_2O_5V$.



$C_{40}H_{28}N_4O_6V_2$

Table -3: The electronic Spectra and the magnetic moment of the Schiff bases and their vanadyl complexes.

The complex	λ nm	ε $Lmol^{-1}cm^{-1}$	ν cm^{-1}	μ_{eff} B.M	Transitions
$C_{40}H_{28}N_2O_2.2H_2O$	263	0.533	38022	-	$*\pi \rightarrow \pi$
$C_{13}H_{11}NO_2$	257	0.678	38910	-	$*\pi \rightarrow \pi$
$C_{20}H_{16}N_2O_2$	207	2.030	48309	-	$*\pi \rightarrow \pi$
$C_{20}H_{18}N_2O_4$	210	1.067	47619	-	$*\pi \rightarrow \pi$
$C_{80}H_{56}N_4O_6V_2$.$5H_2O$	845 445 368	2.294 1.345 0.864	11834 22471 27173	1.2	$^2B_2 \rightarrow {}^1A_1$ $^2B_2 \rightarrow E$ INCT
$C_{26}H_{20}N_2O_5V.2H_2O$	760 480 320	2.461 2.274 0.361	13157 20833 31250	1.65	$^2B_2 \rightarrow {}^1A_1$ $^2B_2 \rightarrow E$ INCT
$C_{40}H_{28}N_4O_6V_2$.$2H_2O$	749 430 305	1.056 2.292 0.930	13351 23255 32786	1.8	$^2B_2 \rightarrow {}^1A_1$ $^2B_2 \rightarrow E$ INCT
$C_{20}H_{16}N_2O_5V$.$3H_2O$	785 510 290	2.249 2.063 0.963	12738 19607 34482	1.76	$^2B_2 \rightarrow {}^1A_1$ $^2B_2 \rightarrow E$ INCT

INCT= Intraligand charge transfer band.

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