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Synthesis, Spectroscopic and Thermal Studies of Vanadyl-N,N′-o-phenylenebis(salicylideneiminato) Complexes

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Two new complexes [V(O)(sal-o-phdn)(H_2O)] and [V(O)(sal-o-phdn)(C_2H_5OH)] (sal-o-phdn = N,N′-o-phenylenebis(salicylideneiminato)) have been synthesized and characterized by elemental and thermal analysis and electronic, infrared and Raman spectra. Both complexes are in the mononuclear forms where the Schiff base occupies the four equatorial positions and H_2O or C_2H_5OH are axially coordinated to the vanadyl oxygen forming distorted octahedral with C_S symmetry. The characteristic ν(V=O) vibrations for the mononuclears are observed at 978 and 981 cm^{-1} for the H_2O and C_2H_5OH complexes, respectively. Full vibrational assignments for all observed bands are made. The vibrations of the coordinated H_2O in [V(O)(sal-o-phdn)(H_2O)] are observed at 3255, 1704, 829 and 645 cm^{-1} while those for the C_2H_5OH in [V(O)(sal-o-phdn)(C_2H_5OH)] are shown at 3620, 2950, 1386 and 860 cm^{-1}.

Key words: vanadyl complexes, N,N′-o-phenylenebis(salicylideneiminato), infrared, thermal

The coordination chemistry of vanadium has attracted considerable attention due to its biological effects based on the recent discovery of two important types of vanadium dependent enzymes [1–3]. One catalyzing the reduction of dinitrogen to ammonia and the other catalyzing the peroxide-dependent halogenation of organic compounds. In addition, some Schiff base complexes may be used as model molecules for biological oxygen carrier systems [4].

Tetradentate Schiff base complexes are well known to form stable complexes, where the coordination takes place through the N_2O_2 donor set [5–7]. However, detailed vibrational and thermal studies on this class of compounds appear to be limited in the literature whilst the Raman spectra are known for few systems. In this paper, we report the synthesis of the two new complexes [V(O)(sal-o-phdn)(H_2O)] and [V(O)(sal-o-phdn)(C_2H_5OH)] (sal-o-phdn = N,N′-o-phenylenebis(salicylideneiminato)). Their resonance Raman, infrared and electronic spectra were recorded and fully assigned along with the complexes thermal properties. This enabled us to characterize the complexes and to explain their bonding and structures.

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EXPERIMENTAL

Analytical reagent grade chemicals were used throughout. The Schiff base N,N′-o-phenylenebis (salicylideneimine) (sal-o-phdnH_2) was prepared from the condensation of o-phenylenediamine with salicylaldehyde in chloroform as a solvent, following the known method [8] and characterized through its infrared spectrum. The oxovanadium(IV) complex [V(O)(sal-o-phdn)(H_2O)] was prepared *via* the reaction of the hydrated vanadyl chloride, $V(O)Cl_2 \cdot 6H_2O$ with the Schiff base sal-o-phdnH_2 in a molar ratio of 1:1, using acetone as a solvent with stirring at *ca.* ~ 45°C temperature. The dark green precipitate was left to cool to room temperature, filtered off, washed with acetone, and dried in a vacuum over P_2O_5. The second complex [V(O)(sal-o-phdn)(C_2H_5OH)], which has a pale green color, was prepared in a similar way to that of the first complex, but using ethanol as a solvent. The two formed complexes were characterized by their elemental and thermal analysis as well as their vibrational spectra. Analysis, [V(O)(sal-o-phdn)(H_2O)]: C, 60.62 (60.15); H, 4.21 (4.01); N, 7.52 (7.02); V, 12.29% (12.78%); [V(O)(sal-o-phdn)(C_2H_5OH)]: C, 61.33 (61.83); H, 4.42 (4.68); N, 6.85 (6.56); V, 11.72% (11.94%), the calculated values are shown in parentheses. The (C, H, N) analysis were preformed at the microanalytical center, UMIST, England, while vanadium was determined gravimetrically.

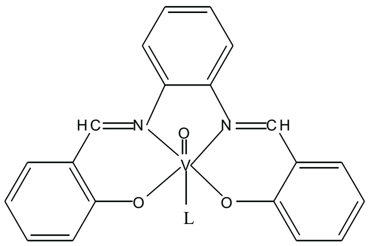
Spectroscopic and thermal measurements. The mid and far infrared spectra of the Schiff base sal-o-phdnH_2 and the complexes [V(O)(sal-o-phdn)(L)] (L= H_2O or C_2H_5OH) were recorded from CsI discs using Nicolet FT-IR, model 670 (4000–400 cm^{-1}) and Nicolet FT-IR, model 760 Magna (600–50 cm^{-1}) spectrometers. The Raman spectrum of [V(O)(sal-o-phdn)(C_2H_5OH)] was measured with a Jobin-Yvon spectrometer using argon excitation line 488.0 nm. To prevent decomposition by the laser beam, the sample (as a pressed disc, 10% by weight in KBr) was examined in a rotating solid disc of conventional design. The electronic absorption spectra of the reactants and the product complexes were measured using a Perkin-Elmer double beam spectrometer model EZ-210. Thermal gravimetric analysis (TG) and (DTG) of the product complexes [V(O)(sal-o-phdn)(L)] (L= H_2O or C_2H_5OH) were carried out using a Perkin-Elmer TGA-7 computerized thermal analysis system. The rate of heating of the samples was kept at 5°C min^{-1} under a N_2 flow at 20 mL min^{-1}. $CuSO_4 \cdot 5H_2O$ was used as a calibrating standard material.

RESULTS AND DISCUSSION

The Schiff base N,N′-o-phenylenebis(salicylideneimine) (sal-o-phdnH_2) reacts with $V(O)Cl_2 \cdot 6H_2O$ in acetone or ethanol to form the corresponding vanadyl complexes [V(O)(sal-o-phdn)(H_2O)] and [V(O)(sal-o-phdn)(C_2H_5OH)] (Scheme 1). The compositions of these two complexes are based on elemental analysis which agree quite well with the 1:1:1 (V(O): Schiff base:H_2O or C_2H_5OH) stoichiometry, as well as on vibrational spectra and thermal properties. Figure 1 shows the Raman spectrum of the complex [V(O)(sal-o-phdn)(C_2H_5OH)]. Table 1 gives the infrared bands for the Schiff base (sal-o-phdnH_2), and the two complexes [V(O)(sal-o-phdn)(L)] (L= H_2O or C_2H_5OH) as well as the Raman bands for the C_2H_5OH complex along with their assignments. Before explaining such assignments, the structures of the two complexes under study must first be discussed.

Chatterjee *et al.* [9] reported the structure of the related vanadyl complexes [V(O)(DPA)(o-phen)] and [V(O)(DPA)(H_2O)$_2$] (DPA = dipiclonic acid). They indicated that the complexes are six coordinated where the three ONO donor atoms of DPA and N of o-phen or O of H_2O occupy the four equatorial positions, while the vanadyl oxygen and the other N of the o-phen or O of the second H_2O are axially coordinated forming distorted octahedral structures. Accordingly, the most probable

Scheme 1



[V(O)(sal-o-phdn)(L)] (L= H_2O or C_2H_5OH)

structure for our complexes [V(O)(sal-o-phdn)(L)] (L= H_2O or C_2H_5OH) is shown in Scheme 1, where the four donor atoms N_2O_2 of the Schiff base are coordinated to V(IV) in a plane with the vanadyl oxygen and the oxygen of H_2O or C_2H_5OH are axially coordinated and perpendicular to this plane forming a distorted octahedral geometry. Similar related H_2O, C_2H_5OH, and DMF complexes of some uranyl Schiff base complexes were previously reported by one of us and others [5,10].

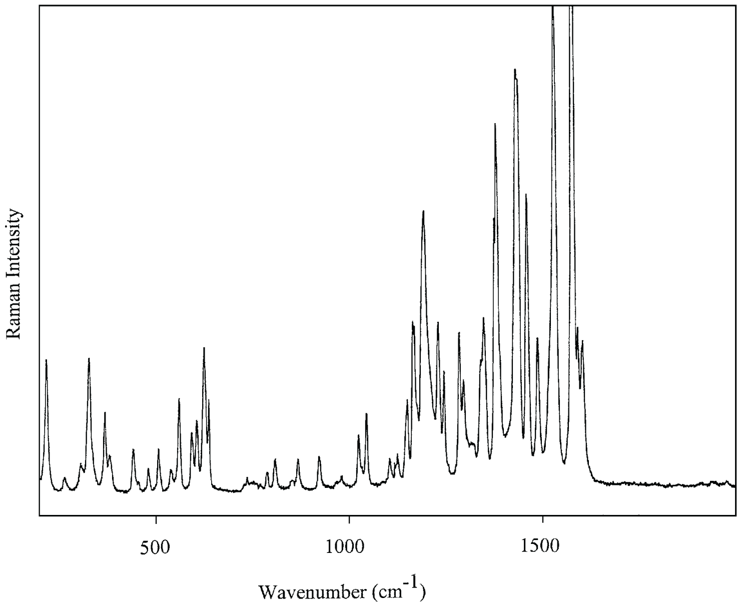


Figure 1. Raman spectrum of [VO(sal-o-phdn)(C_2H_5OH)].

Under this structure, each of the vanadyl complexes has no symmetry elements except for a plane of symmetry and therefore, the species may belong to the C_s symmetry. In such a case, the vibrations of each of the complexes are distributed between motions of the type A′ and A′′, all are monodegenerate and infrared and Raman active. This conclusion is strongly supported by the fact that the measured infrared and Raman spectra for [V(O)(sal-o-phdn)(C_2H_5OH)] are almost the same, Table 1.

Table 1. Infrared and Raman spectra (cm^{-1}) and band assignments of the Schiff base (sal-o-phdnH$_2$) and its complexes [V(O)(sal-o-phdn)(H$_2$O)] and [V(O)(sal-o-phdn)(C$_2$H$_5$OH)].

cm$^{-1(a)}$				
(sal-o-phdnH$_2$)	[V(O)(sal-o-phdn)(H$_2$O)]	[V(O)(sal-o-phdn)(C$_2$H$_5$OH)]		Assignments$^{(b)}$
(IR)	(IR)	(IR)	(Raman)$^{(c)}$	
–	–	3620 w	–	ν(O–H); ROH
–	3432 mw	3444 mw	–	ν(O–H); H_2O, KBr
–	3255 mw	–	–	ν(O–H); coord. H_2O
3044 mw	3056 mw	3055 mw	–	ν(C–H); aromatic
–	–	2950 w	–	ν(C–H); C_2H_5 of ROH
–	1704 mw	–	–	$\delta(H_2O)$; coord. H_2O
1611 vs	1604 vs	1603 vs	1605 wm	ν(C=N)
1561 s	1578 s	1576 s	1576 vs	
–	1535 vs	1532 vs	1529 s	Phenyl breathing modes
1478 s	1495 w	1494 w	1486 m	(quadrant vibrations), and
–	1460 ms	1459 ms	1458 m	CH deformations
–	1437 m	1434 m	1434 m	
–	–	1386 m	1383 m	ν(C–O); ROH
1361 mw	1379 s	1374 m	1374 w	
–	1316 ms	1315 sm	–	
–	–	–	1284 m	
1272 s	1276 m	1252 mw	1244 mw	
–	1232 mw	1233 mw	1228 mw	ν(C–O), ν(C–C) and
1189 s	1198 m	1192 sm	1193 m	ν(C–O), chelating ring
1150 m	1149 m	1148 m	1146 wm	
–	1126 m	1124 wm	1122 w	
–	1028 wm	1029 w	1031 wm	
–	978 s	981 s	980 w	ν(V=O)
–	927 mw	925 mw	923 w	in plane CH-deformation;
905 ms	873	–	–	phenyl
–	–	860 mw	865 w	CH-deformation; ROH
–	829 m	–	–	$\delta_r(H_2O)$; rocking
–	810 wm	811 m	806 w	in plane CH-deformation;
755 vs	752 vs	751 s	759 w	phenyl
–	645 m	–	–	$\delta_w(H_2O)$; wagging
631 mw	624 mw	626 m	623 mw	in plane CH-quadrant
578 mw	563 w	564 wm	561 wm	deformations; phenyl
–	541 ms	542 sm	540 w	ν_{as}(V–O); O of Schiff base
–	–	508 wm	504 w	ν_s(V–O); O of Schiff base

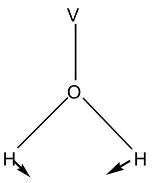
Table 1 (continuation)

471 mw	486 m	484 wm	481 w	out of plane CH-quadrant
436 wm	446 mw	444 w	443 w	deformations; phenyl
–	392 m	–	–	ν(V–O); O of H_2O
373 mw	383 m	389 mw	384 w	out of plane CH-quadrant deformation; phenyl
–	357 mw	–	366 wm	ν(V–N)
330 m	–	–	327 wm	out of plane CH-quadrant
302 mw	306 m	–	305 w	deformations; phenyl
–	–	280 mw	276 w	ν(V–O); O of ROH

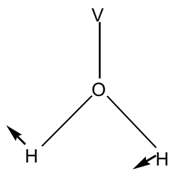
a: s, strong; m, medium; v, very and w, weak. b: ν, bond stretching; δ, angle deformation. c: Raman spectrum was recorded in the 200–2000 cm^{-1} region.

Band assignments. The observed bands of the two vanadyl complexes were assigned, Table 1, based on the spectral intensities, symmetry considerations outlined above and by comparison with literature data for related compounds. The spectra of both complexes display almost the same bands of the Schiff base but, they differ in the characteristic bands for coordinated H_2O or C_2H_5OH. The ν(V=O); A$'$ vibrations are observed as strong infrared bands at 978 and 981 cm^{-1} for the H_2O and C_2H_5OH complexes respectively, while this vibration is observed in the Raman spectrum of the later complex at 980 cm^{-1}. The observation of ν(V=O) around 980 cm^{-1} agrees with the presence of mononuclear oxovanadium species [7,11].

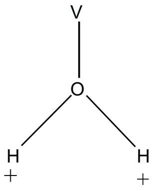
Under the C_s symmetry, the V–OH_2 unit in [V(O)(sal-o-phdn)(H_2O)] should display 6 vibrations and these are 4A$'$ + 2A$''$ corresponding to ν(V–O); A$'$, ν_s(O–H); A$'$, ν_{as}(O–H); A$''$, δ_b(H_2O); A$'$, δ_r(H_2O); A$''$ and δ_w(H_2O); A$'$. These angular deformation motions, δ, are described as follows.



δ_b(bend)



δ_r(rock)



δ_w(wag)

The bands of coordinated H_2O in [V(O)(sal-o-phdn)(H_2O)] occur at 3255, 1704, 829 and 645 cm^{-1} assigned to ν_{as}(O–H), δ_b(H_2O), δ_r(H_2O) and δ_w(H_2O), respectively. These bands do not exist in the spectrum of the [V(O)(sal-o-phdn)(C_2H_5OH)] complex. Instead, the spectrum of this complex shows bands characteristic to coordinated ethanol at 3620, 2950, 1386 and 860 cm^{-1} assigned to ν(O–H), ν(C–H), ν(C–O), and CH-deformation, respectively. The ν(C–H) of the phenyl groups in both complexes occurs around 3055 cm^{-1}. The azomethine stretch, ν(C=N) is observed in the complexes around 1605 cm^{-1}. This motion occurs in the free Schiff base at 1611 cm^{-1}. This shift to lower value upon coordination to V(IV) is normal due to the increase of the reduced mass of the C=N bond. The breathing vibrations of the phenyl groups are assigned to the group of bands in the region 1580–1434 cm^{-1}. The group of bands at 1380–1030 cm^{-1} are related to C–O, C–C and C–N bond stretches of chelate ring. The phenyl CH deformation vibrations occur around 925–735 cm^{-1} and the in-plane CH quadrant deformations are associated with the bands in the region 625–565 cm^{-1}. The phenyl out of plane CH quadrant deformations are assigned to the bands, which occur in 485–445 cm^{-1} region. The expressions developed by Colthup *et al.* [12] were used in the above mentioned assignments.

The ν(V–O) (oxygen of sal-o-phdn) occur in both complexes around 540 cm^{-1}, Table 1, while the corresponding ν(V–O) (oxygen of H_2O or C_2H_5OH) are related to the bands at 392 and 280 cm^{-1}, respectively. The corresponding ν(V–N) vibrations occur at 357 and 366 cm^{-1}. The ν(V–N) vibrations occur at relatively low wavenumber values compared to ν(V–O) in agreement with the fact that, in Schiff base complexes, the V–O bond is stronger than the corresponding V–N bond [13].

The electronic absorption spectra of the complexes, each show three absorptions around 400, 316 and 241 nm, while the spectrum of the free Schiff base shows only two absorptions around 328 and 270 nm. The new band in the complex spectra at 400 nm should be related to the d→d electronic transition, while the 316 and 241 nm absorptions could be assigned to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ electronic transitions, respectively.

To confirm the compositions and structures of the complexes under investigation, thermal gravimetric analysis measurements (TG) and (DTG) were carried out. The thermograms of [V(O)(sal-o-phdn)(H_2O)] is given in Figure 2. It shows the first degradation step at a maximum of 211°C and is accompanied by a weight loss of 4.60%, which corresponds to the loss of one coordinated H_2O in agreement with the theoretically calculated loss of 4.51%. The second stage of decomposition occurs at 418°C due to the loss of one phenyl fragment. The calculated weight loss of this step is 19.05% close to the found value of 18.50%. The final stage of decomposition occurs with a broad structures centered at 558℃ and 623℃. The total weight loss accompanying this step was 52.20% attributed to the loss of two Ph-CH=N fragments. This loss is very close to the theoretical weight loss of 51.62%. The weight found for the residue after decomposition corresponds to about 20% due to the formation of VO_2 close to the calculated weight of 20.80%. The thermogram of [V(O)(sal-o-phdn)(C_2H_5OH)] is similar to that of [V(O)(sal-o-phdn)(H_2O)] except that the loss of C_2H_5OH takes place at 265°C instead of 211°C for H_2O. The other degradations occur around 400, 539 and 620℃ close to those of the H_2O complex and give a weight of the VO_2 residue of 20.10% close to the calculated value of 19.44%.

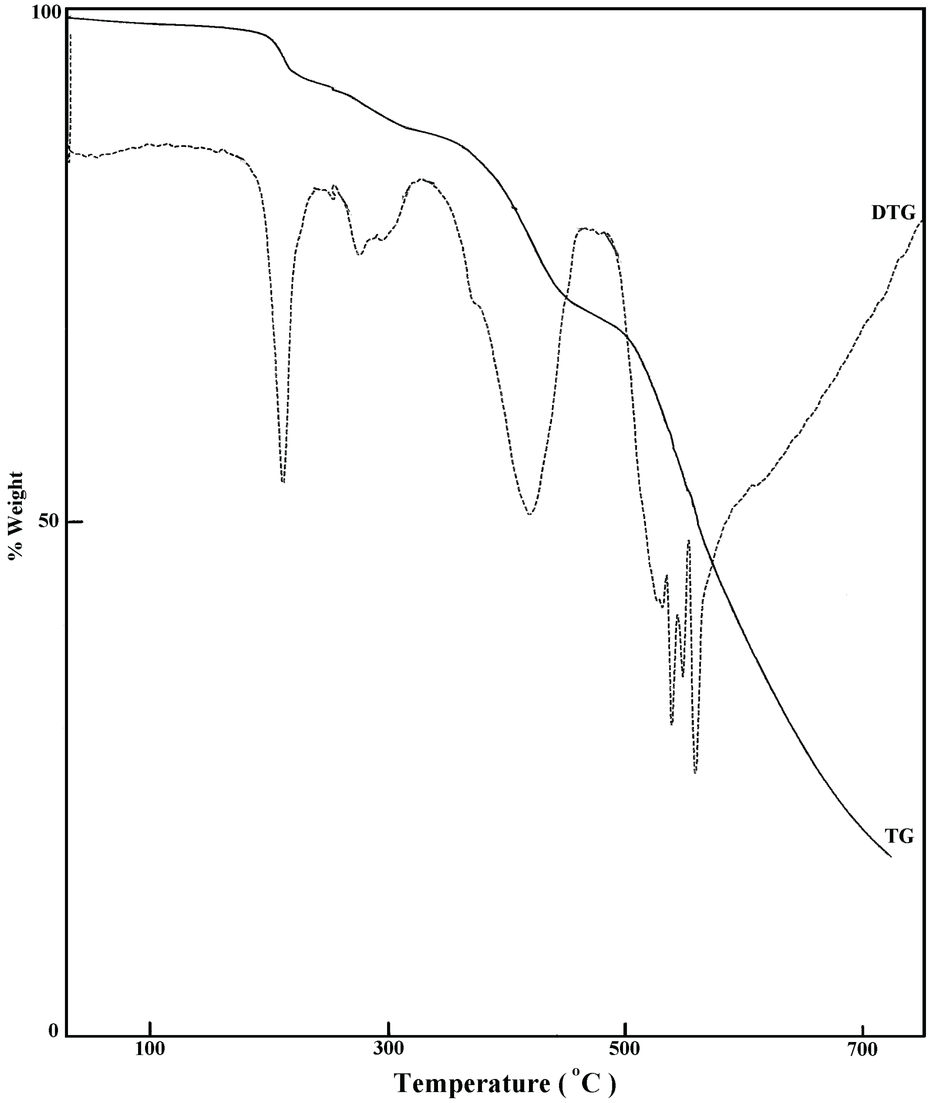


Figure 2. TG and DTG thermal diagrams of [VO(sal-o-phdn)(H_2O)].

CONCLUSIONS

Vanadyl salts react with the Schiff base N,N′-o-phenylenebis(salicylideneimine) (sal-o-phdnH_2) in the solvents acetone or ethanol to form the complexes [V(O)(sal-o-phdn)(H_2O)] and [V(O)(sal-o-phdn)(C_2H_5OH)], respectively. Both complexes are in the mononuclear form with distorted octahedral structures, where H_2O or C_2H_5OH are axially coordinated to the vanadyl oxygen.

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