The net result is reaction 3.

Although an Os(VI) species is the supposed product of Os(VI) ester hydrolysis, H_2OsO_4 (or $OsO_3{\cdot}nH_2O$) has never been positively identified.[13] On the other hand, Os(VI) salts such as potassium osmate, $K_2[OsO_2(OH)_4]$, are well-known. It is with these precautions that we put forward Os(VI) as a key intermediate in the oxidation process.

As mentioned in the Results, we found electrochemical evidence of a reaction between osmium tetroxide and osmium dioxide. This reaction might be a comproportionation to Os(VI).[14] The latter species is invoked as an oxidizing agent for the hydrazinium cation. The sum of reactions 9 and 10 accounts for the autocatalytic activity of osmium dioxide.

$$OsO_4 + OsO_2 + 12H^+ \rightarrow 2Os(VI) + 6H_2O \quad (9)$$

$$2Os(VI) + N_2H_5^+ + 4H_2O \rightarrow 2OsO_2 + N_2 + 13H^+ \quad (10)$$

Integration of the autocatalytic rate law $d[N_2]/dt = k[OsO_2][OsO_4]$ requires knowledge of the initial concentration of osmium dioxide, $[OsO_2]_0$,[15] which can only be estimated. For the initial conditions of Figure 2 and with an estimated $[OsO_2]_0 = 1 \times 10^{-5}$ M, we find $k = 6 \pm 1\ M^{-1}\ s^{-1}$.

Regeneration of osmium tetroxide can be brought about by reduction of chlorate to hypochlorite. No doubt chlorite is an intermediate in reaction 11; however, the much faster reaction

$$OsO_2 + ClO_3^- + H^+ \rightarrow OsO_4 + HClO \quad (11)$$

of hypochlorite with the hydrazinium cation compared with reaction 4 suggests the following step is more significant:

$$2HClO + N_2H_5^+ \rightarrow 2Cl^- + N_2 + 2H_2O + 3H^+ \quad (12)$$

The sum (3) + (9) + (10) + 2(11) + (12) equals the stoichiometry of overall reaction 1.

Reactions 3 and 9-12 comprise our mechanism for the osmium tetroxide catalyzed hydrazinium cation-chlorate reaction. Rate constants for these steps are not reported in the literature. Some of the reactions might be amenable to study via spectroscopic and stopped-flow techniques, provided interference from colloidal osmium dioxide and nitrogen gas can be minimized. The overall reaction with chlorate could produce exotic nonlinear dynamics in an open (flow) reactor, and we expect to continue its study under these conditions.

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Contribution from the Department of Chemistry,
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Reinvestigation of the Vanadium-Oxygen Stretch in the IR Spectrum of Bis[*N*-(4-chlorophenyl)salicylideneaminato]oxovanadium(IV)

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Introduction

Oxovanadium(IV) complexes have been extensively studied.[1-3] Most of these complexes exhibit a strong band in the IR region near 1000 cm^{-1}, which has been assigned to the V=O stretching frequency.[1,2] In contrast, several complexes have been reported[4-12] in which this stretch appears at lower energy—below 900 cm^{-1}. This shift has been explained in terms of polymerization, which occurs by interaction of the vanadyl oxygen in one molecule with the open axial site of vanadium in another molecule,[6-10] and Mathew et al. suggested that a low-frequency V-O stretch may be a diagnostic test for oxygen bridging in vanadyl complexes.[8] However, in 1977 Pasquali, Marchetti, and Floriani reported an oxovanadium(IV) compound with a V-O stretch of 885 cm^{-1} whose crystal structure revealed monomeric units.[11] They explained the shift in the V-O stretch of this compound in terms of electron withdrawal by chlorine on the ligand and cautioned against using the frequency of the V-O stretch to infer whether or not polymerization of the type described above is present. Reported here is a reinvestigation of the infrared spectrum of the vanadyl complex reported by Pasquali et al.[11] It is shown that two forms of this compound exist, the monomeric form, reported by Pasquali et al., and a form which is apparently polymeric.

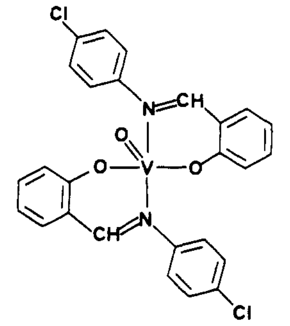

Figure 1. V(O)L_2.

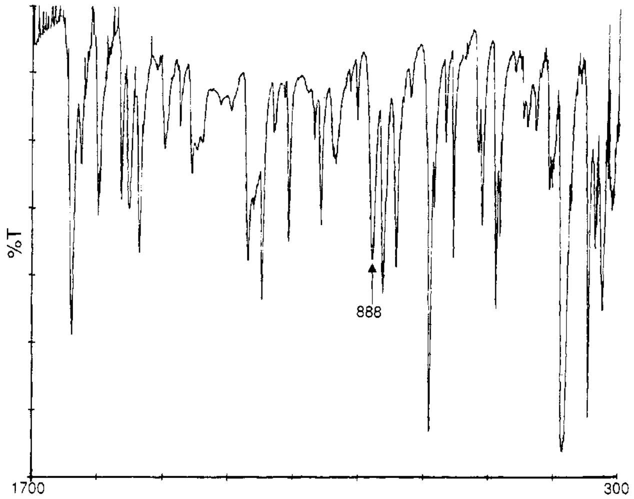

Figure 2. IR spectrum for the needle form of V(O)L_2.

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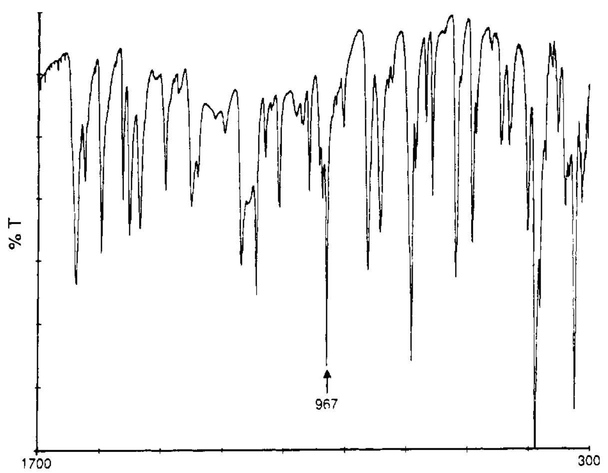

Figure 3. IR spectrum for the prism form of $V(O)L_2$.

Infrared spectra of both forms are presented, and show that the previous workers were in error in their assignment.

Experimental Section

Bis[*N*-(4-chlorophenyl)salicylideneaminato]oxovanadium(IV) was prepared according to the procedure of Pasquali et al.[11] A yellow-brown solid was initially produced; upon recrystallization from carbon disulfide both yellow-brown prisms and needles were obtained, with the needle form predominating. Samples of the prism form and needle form were obtained by carefully separating individual crystals from the mixture and were sent for elemental analysis. Anal. Calcd for $VC_{26}H_{18}N_2O_3Cl_2$: C, 59.11; H, 3.43; N, 5.30; Cl, 13.42. Found (needle form): C, 57.91;[13] H, 3.41; N, 5.24; Cl, 13.41. Found (prism form): C, 59.13; H, 3.53; N, 5.25; Cl, 13.35.

Unit cell parameters of the prism form were obtained by mounting a suitable crystal on a Syntex P3 automated diffractometer. Least-squares refinement of the best angular positions for 10 independent reflections ($2\theta > 18°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å) yielded a monoclinic cell with $a = 10.973$ (6) Å, $b = 20.944$ (34) Å, $c = 9.931$ (9) Å, and $\beta = 99.50$ (6)°.

Infrared spectra of both the prism form and needle form in the solid state were recorded on a Nicolet 20 DXC Fourier-transform infrared spectrometer, using a Spectratech Model 300 continuously variable ATR attachment. Samples were finely ground and then mounted with double-sided tape. An angle of 60° was used to minimize interference by the tape. An IR spectrum was recorded for a carbon disulfide solution with the use of sodium chloride cells. Elemental analyses were performed by the Microanalysis Laboratory at the University of Massachusetts, Amherst, MA.

Results

Synthesis of bis[*N*-(4-chlorophenyl)salicylideneaminato]oxovanadium(IV), subsequently referred to as $V(O)L_2$ (Figure 1), led to formation of both fine yellow-brown needles and brown prisms. The two forms were manually separated, and their IR spectra were recorded (Figures 2 and 3). The IR spectra of the two products are very similar between 1700 and 600 cm^{-1}, differing only in the position of the V–O stretch. For the needle form, a peak at 888 cm^{-1} can be assigned to this stretch. This agrees with the value of 885 cm^{-1} reported by Pasquali et al.[11] However, the IR spectrum of the prism form lacks this feature; instead, an intense peak at 967 cm^{-1} can be assigned to the V–O stretch. Minor differences in peak intensities are observed in the spectra below 650 cm^{-1}, where V–O and V–N stretches of the Schiff-base ligand occur.[4] Near 355 cm^{-1} there is a moderately strong peak present in the spectrum of the needle form, while the spectrum of the prism form shows two less intense peaks. The IR spectrum recorded for a carbon disulfide solution of the unseparated product mixture is also similar to the spectra recorded for the solid forms, except for peaks which may be assigned to the V–O stretch. In the solution spectrum there is no peak at either 967 or 888 cm^{-1}, but there is a peak at 988 cm^{-1} which is not present in the spectra recorded for the two solids.

Discussion

The unit cell parameters determined for the prism form isolated in this study ($a = 10.973$ (6) Å, $b = 20.944$ (34) Å, $c = 9.931$ (9) Å, and $\beta = 99.50$ (6)°) are in good agreement with values reported by Pasquali et al.[11] ($a = 11.08$ (2) Å, $b = 21.14$ (3) Å, $c = 10.06$ (2) Å, and $\beta = 99.0$ (2)°), indicating that the prism form of the product has the same structure as the form they reported. This form is monomeric and contains a vanadium which is five-coordinate.

The value for the V–O stretch of the prism form determined in this work, 967 cm^{-1}, falls in the range generally accepted for the vanadium–oxygen stretch in five-coordinate oxovanadium(IV) complexes, 910–1035 cm^{-1}.[1,2] This is quite different from the value reported by Pasquali et al. for the V–O stretch. It is possible that although the crystal structure reported by Pasquali et al. was of a single crystal of the monomeric prism form, their IR spectrum was recorded on the unseparated mixture obtained after recrystallization, which contains mostly the needle form, with the assumption that the structure of the needles was the same as that of the crystal used to obtain the structural data. Since the needle form predominated, they observed the V–O stretch at 885 cm^{-1}. In this study, the V–O stretch of the needle form was observed at 888 cm^{-1}. A shift in the V–O stretching frequency to below 900 cm^{-1} has been considered an indication of oxygen-bridging, V–O–V polymerization.[7-10] Therefore it seems likely that the needle form of $V(O)L_2$ is such a polymer. In carbon disulfide the product shows a V–O stretch at 988 cm^{-1}, indicating that the complex is monomeric in solution.

Thus it seems that the suggestion of Mathew et al.[8] that a low-frequency V–O stretch serve as a diagnostic test for oxygen bridging in vanadyl complexes is valid, since Pasquali et al.[11] were mistaken in their assignment of a V–O stretch for a monomeric, five-coordinate complex at 885 cm^{-1}.

Acknowledgment. I thank Joanne Stewart of Hope College for drawing my attention to this problem.

Registry No. $V(O)L_2$, 32065-25-1; $[V(O)L_2]_x$, 132014-35-8.

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[13] In the presence of vanadium, carbon analyses may be depressed due to formation of vanadium carbide. Therefore this value is lower than the true value.

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Reaction of $Rh_2(\mu\text{-}SO_2)Cl_2(\mu\text{-dppm})_2$ with Trimethylphosphine and Nitrosonium Tetrafluoroborate: Solid-State Structures of $[Rh_2(\mu\text{-}Cl_2)(NO)_2(\mu\text{-dppm})_2](BF_4)_2$ and $RhCl(PMe_3)(dppm)$

Yuan-Wen Ge and Paul R. Sharp*

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Introduction

Bridging bis(diphenylphosphino)methane (dppm) and bis(dimethylphosphino)methane (dmpm) complexes of Rh and Ir constitute a large area of bimetallic chemistry. The entry points for most of this chemistry are the face-to-face complexes $M_2(CO)_2Cl_2(\mu\text{-}L_2)_2$ (M = Ir or Rh, L_2 = dppm or dmpm).[1] These complexes are versatile synthetic precursors and have been used to prepare a diverse range of complexes.[1,2]

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