found possible to convert $Na_5[Fe(H_2IO_6)_2(OH)_2]$ to $H_3[Fe_4I_3O_{24}H_{12}]$. Qualitatively, it was shown that addition of acid to the 1:2 complex caused it to change color from yellow-green to the characteristic ochre of the 4:3 complex. The mother liquor gave a white precipitate with tetraphenylarsonium chloride, indicative of free periodate. A semiquantitative experiment showed that the amount of periodate liberated on acidification of the 1:2 complex was in good agreement with that expected theoretically. Two 0.194-g. samples of the 1:2 complex were taken, acidified with 10 ml. of 1 *N* H_2SO_4, and allowed to stand for 24 hr. The 4:3 complex was filtered off, and to the filtrate (*ca.* 500 ml.) at about 80° was added 35 g. of NaCl, making the solution about 1.5 *M* with respect to the latter. A 50% excess of tetraphenylarsonium chloride solution (20 ml. of a solution of 1 g. in 100 ml.) was added slowly with stirring. The precipitate was filtered (after the solution had stood overnight) and dried at 110°. The amount of IO_4^- found in both instances was 0.073 g., and the amount which theoretically would be liberated if the reaction proceeded stoichiometrically was 0.071 g. The discrepancy is well within experimental error and the results indicate conversion according to the equation

$$4Na_5[Fe(H_2IO_6)_2(OH)_2] + 15H^+ \longrightarrow H_3[Fe_4I_3O_{24}H_{12}] + 5IO_4^- + 20Na^+ + 12H_2O$$

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The Preparation and Properties of Some Oxovanadium(IV) Complexes

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The preparation of the complexes $VO(ClO_4)_2 \cdot 5C_5H_5NO$, $VOCl_2 \cdot 2(C_6H_5)_3PO$, $VO(ClO_4)_2 \cdot 4(C_6H_5)_3PO$, $VOCl_2 \cdot 4(C_6H_5)_3AsO$, $VO(ClO_4)_2 \cdot 4(C_6H_5)_3AsO$, and $VOCl_2 \cdot 3(CH_3)_2SO$ are reported. Arguments for structural assumptions are based upon measurements of their visible and infrared spectra, magnetic moments, and conductances in polar solvents.

Introduction

In an extension of earlier work with oxygen donor species[1-3] we attempted to prepare some addition compounds of vanadium(III). In each case the product was a complex of VO^{2+} ion, when atmospheric oxygen was not excluded during the syntheses. While the preparative work with VO^{2+} complexes was going forward, Ballhausen and Gray[4] reported a detailed analysis of the electronic spectrum of the vanadyl ion based on a molecular orbital model, in contrast to Jørgensen's[5] analysis based on simple tetragonal distortion of a cubic crystal field.

Experimental

Reagents.—Reagent grade chemicals were used without further purification except in the cases noted.

Methylene chloride, used as a solvent for spectral measurements, was dried over calcium chloride and saturated with dry nitrogen.

Triphenylarsine oxide and triphenylphosphine oxide were prepared by similar procedures[6] from Eastman "White Label" triphenylarsine and triphenylphosphine, respectively. Pyridine N-oxide, obtained from K and K Chemical Company, was purified by vacuum distillation and stored in a moisture-free container.

Vanadium(III) chloride 6-hydrate was a student preparation.[7]

Analyses.—The complexes were decomposed for vanadium analyses by digestion with a mixture of concentrated H_2SO_4, HNO_3, and $HClO_4$. The digested sample was diluted to volume, treated with 30% H_2O_2, allowed to

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(1) S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 122 (1962).

(2) D. J. Phillips and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 1806 (1961).

(3) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, Jr., *ibid.*, **83**, 3770 (1961).

(4) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(5) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1957).

(6) R. L. Shriner and C. N. Wolf, *Org. Syn.*, **30**, 97 (1950).

(7) G. Brauer, "Handbuch der Praparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954, p. 945.

stand, and the optical density of the solution read on a Beckman DU spectrophotometer.[8]

Samples for chloride and perchlorate analyses were fused with a sodium peroxide–sucrose–potassium nitrate mixture in a Parr bomb.[9] The fused melt was dissolved in water, acidified, and filtered. The chloride present was precipitated with $AgNO_3$ solution and determined gravimetrically as AgCl. Alternatively, chloride analyses were performed by digestion of the sample with fuming HNO_3 in the presence of solid $AgNO_3$, and weighing the AgCl.

Nitrogen analyses were performed by the micro-Dumas method.[10]

Arsenic analyses were carried out by digestion of the sample in concentrated H_2SO_4, HNO_3, and $HClO_4$, followed by reduction with hydrazinium sulfate.[9a] The reduced sample was diluted and titrated with ceric solution.[11]

Carbon and hydrogen analyses were done by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Magnetic Moment Measurements.—Magnetic suseptibilities were determined by the Gouy method, using a permanent magnet as described elsewhere.[1]

Conductance measurements were made at 25° in dimethylformamide solvent, in the manner previously described.[3]

Infrared Spectra.—A Baird Associates recording spectrophotometer, serial number AB2-193, was used. The spectra were measured on mineral oil mulls of the samples between NaCl plates.

Visible Spectra.—The samples were weighed into 25-ml. volumetric flasks, and diluted to volume with CH_2Cl_2 in a nitrogen atmosphere. The concentrations were in the range of 0.01 *M*. The absorbances of the solutions were measured on a double beam Model 14 Cary recording spectrophotometer, using 1-cm. matched silica cells to contain the samples and reference solvent. Measurements were made from 3,000 Å. (where continuous absorption was observed at the concentrations used) to approximately 9,000 or 10,000 Å. At least two, and in most cases three or more, solutions were made up from different preparations of the same complex. The agreement between duplicate determinations of observed adsorption peaks and extinction coefficients was fair. For example, determinations on five solutions from two different preparations of $VOCl_2 \cdot 4(C_6H_5)_3AsO$ gave these results: λ_1 = 7550, 7450, 7450, 7470, 7500 Å.; λ_3 = 3950 in all five cases; ϵ_1 = 33.9, 32.4, 30.4, 32.6, 32.6; ϵ_3 = 36.8, 25.4, 29.2, 25.9, 27.5.

Preparation of Complexes. **$VO(ClO_4)_2 \cdot 5C_5H_5NO$.**—To a warm (30–40°)[12] dark green solution of 0.46 g. of $VCl_3 \cdot 6H_2O$ and 1.2 g. of C_5H_5NO in 40 ml. of ethanol was added a warm solution of 0.84 g. of $LiClO_4 \cdot 3H_2O$ in 20 ml. of ethanol. An emerald green solid separated from the solution. It was washed with ethanol and ether, and dried over P_2O_5 at reduced pressure; m.p. with decomposition, 170°. *Anal.* Calcd. for $VO(ClO_4)_2 \cdot 5C_5H_5NO$: N, 9.45; Cl, 9.56; V, 6.87; C, 40.51; H, 3.40. Found: N, 9.01; Cl, 9.77; V, 7.14; C, 40.65; H, 3.55.

$VOCl_2 \cdot 2(C_6H_5)_3PO$.—A green solution of 0.23 g. of $VCl_3 \cdot 6H_2O$ in 20 ml. of ethanol was added to a warm solution of 1.55 g. of $(C_6H_5)_3PO$ in 20 ml. of ethanol. The resulting light green solution turned blue on standing. Evaporation under reduced pressure caused a blue-green solid to separate. The product was filtered, washed with ethanol, and dried over P_2O_5 at reduced pressure. *Anal.* Calcd. for $VOCl_2 \cdot 2(C_6H_5)_3PO$: Cl, 10.21; V, 7.34; C, 62.27; H, 4.35. Found: Cl, 10.18; V, 7.06; C, 61.25; H, 3.87.

$VO(ClO_4)_2 \cdot 4(C_6H_5)_3PO$.—A green solution of 0.23 g. of $VCl_3 \cdot 6H_2O$ in 20 ml. of ethanol was added to a warm colorless solution of 1.55 g. of $(C_6H_5)_3PO$ and 0.42 g. of $LiClO_4 \cdot 3H_2O$ in 40 ml. of ethanol. The resulting yellow-green solution turned blue on standing, and a finely divided light blue precipitate formed. The product was isolated by centrifugation, washed thoroughly five times with ethanol, and dried over P_2O_5 at reduced pressure. *Anal.* Calcd. for $VO(ClO_4) \cdot 4(C_6H_5)_3PO$: Cl, 5.15; V, 3.70; C, 62.71; H, 4.38. Found: Cl, 5.12; V, 3.74; C, 61.62; H, 4.23.

$VO(ClO_4)_2 \cdot 4(C_6H_5)_3AsO$.—To a warm green solution of 0.23 g. of $VCl_3 \cdot 6H_2O$ and 1.75 g. of $(C_6H_5)_3AsO$ in 50 ml. of ethanol was added 0.42 g. of $LiClO_4 \cdot 3H_2O$ in 20 ml. of warm ethanol. An immediate white precipitate formed, and when all the $LiClO_4$ solution had been added, a finely divided baby-blue powder was the product. It was isolated by centrifugation, washed well five times with ethanol, and dried over P_2O_5 at reduced pressure. The blue powder is insoluble at room temperature in H_2O, concentrated NH_4OH, concentrated HNO_3, acetone, benzene, chloroform, and carbon disulfide. It is slowly dissolved in concentrated HCl and nitrobenzene, leaving a white residue in nitrobenzene. *Anal.* Calcd. for $VO(ClO_4)_2 \cdot 4(C_6H_5)_3AsO$: Cl, 4.56; V, 3.30; C, 55.61; H, 3.90; As, 19.29. Found: Cl, 4.64, V, 3.34; C, 55.60; H, 3.12; As, 20.00.

$VOCl_2 \cdot 4(C_6H_5)_3AsO$.—A green solution of 0.66 g. of $VCl_3 \cdot 6H_2O$ in 20 ml. of ethanol was added to 5.0 g. of $(C_6H_5)_3AsO$ in 20 ml. of ethanol. As the vanadium solution was added to the ligand solution, a color change to violet was observed, rapidly changing to blue-green. On standing a blue solid separated from the solution. The product was filtered, washed with ethanol, and dried in a vacuum desiccator, and then recrystallized from chloroform and dried over P_2O_5 at reduced pressure; m.p. 240–243°. *Anal.* Calcd. for $VOCl_2 \cdot 4(C_6H_5)_3AsO$: Cl, 4.97; V, 3.58; C, 60.61; H, 4.24. Found: Cl, 5.01; V, 3.60; C, 58.14; H, 4.38.

$VOCl_2 \cdot 3(CH_3)_2SO$.[13]—Roughly 1 g. of very wet $VCl_3 \cdot 6H_2O$ was dissolved in 25 ml. of ethanol to give a green solution. Six ml. of $(CH_3)_2SO$ was added, with no color change being observed. The mixture was warmed in air on a hot plate, and allowed to stand in air. The solution turned bright blue on cooling. Further evaporation on the hot plate and subsequent cooling produced a crop of light blue fine crystals, which were filtered, washed with ethanol, and dried over $CaCl_2$ in a vacuum desiccator.

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[8] The procedure used was based on procedures reported by E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2d ed., Interscience Publishers, Inc., New York, N. Y., 1950, p. 609, and by E. R. Wright and M. G. Mellon, *Anal. Chem.*, **9**, 375 (1937).

[9] (a) D. L. Venezky, Dissertation, University of North Carolina, 1962; (b) Parr Instrument Company, Moline, Ill., "Peroxide Bomb Apparatus and Methods."

[10] J. B. Niederl and V. Niederl, "Micromethods of Quantitative Organic Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 79.

[11] G. F. Smith and W. H. Fly, *Anal. Chem.*, **21**, 1233 (1949).

[12] We were careful not to allow the perchlorate solutions in any of the preparations to go above 50°.

[13] Reported previously in a note by J. Selbin, L. H. Holmes, and S. P. McGlynn, *Chem. Ind.* (London), 746 (1961).

TABLE I

Compound	Obsd. M–O frequency M = N, P, As, S (cm.$^{-1}$)	Shift due to coördination (cm.$^{-1}$)	μ effect (Bohr Magnetons)	Λ (ohms^{-1} cm.^{2} mole^{-1})
$VO(ClO_4)_2 \cdot 5C_5H_5NO$	1200	−43	1.75	184
$VOCl_2 \cdot 2(C_6H_5)_3PO$[b]	1140, 1088	−42, −94	1.74	1.2[a]
$VO(ClO_4)_2 \cdot 4(C_6H_5)_3PO$[b]	1090	−92		
$VOCl_2 \cdot 4(C_6H_5)_3AsO$	822	−58	1.76	68.7
$VO(ClO_4)_2 \cdot 4(C_6H_5)_3AsO$	826	−54	1.88	144
$VOCl_2 \cdot 3(CH_3)_2SO$	1015 or 996	−35 or −54	1.76	1.8[a]

[a] Conductance values in nitrobenzene solvent. [b] The absorption peaks attributed to shifted P–O stretching frequencies by Sheldon and Tyree[14] at 1125 cm.$^{-1}$ were actually those corresponding to a C–H wagging motion. The latter is shifted by no more than 5 cm.$^{-1}$ upon complexing.

The product is quite soluble in ethanol, somewhat less soluble in CH_2Cl_2, and extremely hygroscopic. *Anal.* Calcd. for $VOCl_2 \cdot 3(CH_3)_2SO$: Cl, 19.05; V, 13.69; C, 19.36; H, 4.87. Found: Cl, 18.87; V, 13.60; C, 19.81; H, 5.04.

Results

The new complexes prepared are listed in Table I, together with some physical properties. The conductance values are for 0.001 *M* solutions in dimethylformamide. Under the conditions used, 1:1 electrolytes generally have molar conductances downward from 85 ohm^{-1} cm.^{2} mole^{-1} and 2:1 electrolytes fall in the range 140–170 ohm^{-1} cm.^{2} mole^{-1}.[3]

The shifts in M–O stretching frequencies observed upon coördination are included in Table I. The M–O frequencies of the free ligands are assigned as[1]: As–O, 878 cm.$^{-1}$; P–O, 1182 cm.$^{-1}$; N–O, 1243 cm.$^{-1}$ [3]; and S–O, 1050 cm.$^{-1}$. The peaks are shifted to a lower frequency in each case. This should be expected from the lessening of double bond character in the M–O bond upon coördination of the oxygen to the oxovanadium(IV) ion.

In the infrared spectrum of each compound listed in Table I, a strong, sharp band at or near 1000 cm.$^{-1}$ was observed. This band is most certainly the V=O stretching vibration.[13] Clearly the M–O frequency assignments in Table I will not be confused with the V=O stretch, except in the case of the sulfoxide complex. In the latter case, we are unable to distinguish.

The results of the visible spectra study are listed in Table II. The assignments for the observed transitions are based on Ballhausen's molecular orbital model, which is considered in the Discussion section.

Discussion

In all the complexes studied, strong tetragonal distortion of the octahedrally coördinated species is to be expected, since the ion involved is the oxovanadium(IV) ion, VO^{2+}. In all but one compound, the ligands are combinations of Cl^- and various oxygen donor species, creating a ligand field of still lower symmetry than tetragonal. However, since the other deviations from cubic symmetry should be reasonably small compared to the tetragonal distortion, the results are explained using a model which assumes that five of the ligands are alike.

If the assumption is made that the V^{4+} species is hexacoördinated, the variable stoichiometry from one ligand to another is rather surprising. $VO(ClO_4)_2 \cdot 5C_5H_5NO$ seems to be straightforward, with five C_5H_5NO ligands and the vanadyl oxygen occupying the sixth position. Conductance studies indicate that, in dimethylformamide, the arsine oxide complex is a 1:1 electrolyte, existing as $VOCl[(C_6H_5)_3AsO]_4{}^+Cl^-$. It seems reasonable to assume the same species exists in the CH_2Cl_2 solution in which the spectrum was measured. The $(CH_3)_2SO$ complex contains six ligands per vanadium, is a non-electrolyte in nitrobenzene, and is presumably an octahedral complex. However, it is difficult to account for the stoichiometry of the $(C_6H_5)_3PO$–chloride complex. Although analytical methods would not be expected to establish whether the sixth position is occupied by a water molecule, no OH peak was observed in the infrared spectrum. Since the compound was prepared in ethanol, the absence of the OH peak also eliminates the possibility of solvent coördination. As a matter of fact, Jones has shown that only strong, non-sterically hindered bases are able to expand the coördination of vanadium from five to six under these circumstances.[15] It is prob-

[14] J. C. Sheldon and S. Y. Tyree, *J. Am. Chem. Soc.*, **80**, 4775 (1958).

TABLE II[a]

Compound	λ, Å. (shoulder)	ν, cm.⁻¹	ε	Assignment
$VOCl_2 \cdot 4(C_6H_5)_3AsO$	7480	13,400	32.4	$^2B_2 \rightarrow {}^2E(I)$
	(6500)	(15,400)		$^2B_2 \rightarrow {}^2B_1$
	(3950)	(25,300)	29.0	$^2B_2 \rightarrow {}^2A_1$
$VOCl_2 \cdot 3(CH_3)_2SO$	7140	14,000	38.0	$^2B_2 \rightarrow {}^2E(I)$
	(3950)	(25,300)	9.3	$^2B_2 \rightarrow {}^2A_1$
	3750	26,700	10.2	$^2B_2 \rightarrow {}^2A_1$
$VOCl_2 \cdot 2(C_6H_5)_3PO$	7430	13,500	34.8	$^2B_2 \rightarrow {}^2E(I)$
	4000	25,000	9.7	$^2B_2 \rightarrow {}^2A_1$
$VO(ClO_4)_2 \cdot 5C_5H_5NO$	6250	16,000	40.5	$^2B_2 \rightarrow {}^2E(I)$
	(5550)	(18,000)		$^2B_2 \rightarrow {}^2B_1$
	(3600)	(27,800)	92.5	$^2B_1 \rightarrow {}^2A_1$

[a] It should be noted that no ligand field spectra of $VO(ClO_4)_2 \cdot 4(C_6H_5)_3AsO$ and $VO(ClO_4)_2 \cdot 4(C_6H_5)_3PO$ are reported. The latter is insufficiently soluble in the solvents at our disposal, bearing in mind the order of magnitude of extinction coefficients. (Significant conductance measurements can be made using solutions tenfold more dilute.) Attempts to obtain the spectra in KBr pellet form failed, a phenomenon we always observe with perchlorate complexes. We do not have a reflectance attachment for the Cary spectrophotometer at our disposal.

able that, in the solid state, the complex is five-coördinate like VO(acetylacetone)$_2$.[4] Such a structure would result in a molecular energy level diagram not greatly different from those of the six-coördinate structures, in fact of C_{4v} symmetry. This assumption is supported by the similarity of the crystal field spectrum of the $(C_6H_5)_3PO$ complex to those of the hexacoördinated complexes.

The molecular orbital model of Ballhausen and Gray[4] for $VO(H_2O)_5^{2+}$ takes into account π-bonding of the vanadyl oxygen. The pertinent assignments for VO^{2+} complexes studied previously are[4,5]: 13,000 cm.⁻¹, $^2B_2 \rightarrow {}^2E(I)$; 16,000 cm.⁻¹, $^2B_2 \rightarrow {}^2B_1$; and 29,000 cm.⁻¹, $^2B_2 \rightarrow {}^2A_1$.

In three of the complexes studied by us, the first transition was observed at slightly higher energies, 13,500–14,000 cm.⁻¹. The bands were very broad; for example, the half-width δ^+ for the 14,000 cm.⁻¹ band in $VOCl_2 \cdot 3(CH_3)_2SO$ was about 2000 cm.⁻¹. We suggest that the failure to observe the $^2B_2 \rightarrow {}^2B_1$ transition in the $(C_6H_5)_3PO$ and $(CH_3)_2SO$ complexes is partly accounted for by its being hidden under the broad band around 14,000 cm.⁻¹. Also, in the $(C_6H_5)_3AsO$ case, the suggestion of a shoulder occurs at the slightly lower energy of 15,400 cm.⁻¹. We are led to the conclusion that the $^2E(I)$ and $^2B_1$ levels lie somewhat closer together in our complexes than in $VO(H_2O)_5^{2+}$, masking the weaker band. Since the fields created by the mixed Cl^- and oxygen donor ligands have lower than tetragonal symmetry, it is to be expected that the $^2E(I)$ level will be split somewhat, blurring still further the bands corresponding to transitions involving this level.

In the case of $VO(ClO_4)_2 \cdot 5C_5H_5NO$, the transitions to both the $^2E(I)$ and $^2B_1$ states lie at considerably higher energies than with the other ligands, indicative of a stronger ligand field. C_5H_5NO has no greater dipole moment than either $(C_6H_5)_3PO$ or $(C_6H_5)_3AsO$.[16,17] Also its molecular polarization is less than that of $(C_6H_5)_3PO$.[18] Under these circumstances we suggest that the apparent stronger interaction of the C_5H_5NO is due to a more favorable steric factor than with the other three, more bulky ligands. Such a postulate finds support in the work of Jones.[15] An astute referee pointed out that the foregoing steric argument can hardly be valid for the axial ligand, *trans* to the vanadyl oxygen. In this case (as he suggested) weaker interaction as inferred with the aid of references 16–18 would permit greater π-bonding between the V^{4+} and the vanadyl oxygen, giving greater separation between $^2B_2$ and $^2E(I)$.

The $^2B_2 \rightarrow {}^2A_1$ transition, observed in our complexes at 25,000–27,000 cm.⁻¹, is hidden in many VO^{2+} complexes[4] by a charge transfer band setting in at about 30,000 cm.⁻¹. Apparently the $^2A_1$ level lies somewhat lower in our complexes than it does in $VO(H_2O)_5^{2+}$.

The magnetic moments of the complexes are all close to the spin-only value for one unpaired electron, although the value for $VO(ClO_4)_2 \cdot 4(C_6H_5)_3AsO$ is rather high. The conductance value for this complex in dimethylformamide indicates a 2:1 electrolyte; possibly another example of a five-coördinate complex.

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