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Some Complexes of Oxovanadium(IV)

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Complexes of the type $VOX_2.2L$ ($X = Cl^-$, Br^- and NO_3^- and L = a monodentate amide ligand) as well as $VOI_2.5DMSO$ (DMSO = dimethylsulphoxide) and $VOCl_2.2.5CH_3CN$ have been prepared in non-aqueous media. These compounds were all characterised by means of ultraviolet, infrared spectroscopy and conductivity measurements in non-aqueous medium.

Introduction

Complexes of oxovanadium(IV) have been studied extensively in the last decade.[1] According to a recent review no solid nitrate[1a] of this cation has yet been reported and the author presumes that it is unlikely that stable iodides[1b] will ever be prepared. Efforts were made to stabilise oxovanadium(IV) in the presence of nitrate and iodide in non-aqueous media by using strongly basic oxygen donor ligands such as hexamethylphosphoramide (HMPA), NNN'N',tetramethylurea (TMU), dimethylsulphoxide (DMSO), and other amides. A study of amide-complexes of $VOCl_2$ and $VOBr_2$ was also undertaken since only a few amide-complexes of this cation have hitherto been isolated and studied.[1]

Anhydrous $VOCl_2$ was used as starting material for some of the complexes. The existing laborious methods for the preparation[2,3,4] of this compound, namely, either by passing a mixture of $VOCl_3$ vapour and hydrogen gas through a red hot tube or by acting with zinc on $VOCl_3$ in a sealed tube at 400°C, were simplified considerably by treating a concentrated aqueous solution of $VOCl_2$ (which is about 6M with respect to hydrochloric acid) with excess of thionyl chloride, ultimately refluxing under the same solvent for five hours. Upon vacuum drying, the insoluble light green product proved to be new method is somewhat surprising since thionyl chloride was recently found[5] to chlorinate the tetrachlorooxovanadate(IV) species. (This method was used to prepare hexachlorovanadate(IV) salts).

Since pure $VOCl_2.2.5CH_3CN$ could easily be prepared from the impure anhydrous $VOCl_2$, this compound was used as starting material for the preparation of pentakis(dimethylsulphoxide)oxovanadium(IV) iodide and dinitrato-bis(hexamethylphosphoramide)oxovanadium(IV). Both infrared and non-aqueous conductivity data indicated that the nitrate group is bonded covalently to the vanadium. The dark blue, crystalline $VO(NO_3)_2.2HMPA$ is indefinitely stable in a dry atmosphere. When dissolved in water, the nitrate immediately oxidises the vanadium(IV) to vanadium(V).

The blue-green $VO(DMSO)_5I_2$ is slowly oxidised to iodine by dry oxygen, though it is stable in a dry inert atmosphere. When dissolved in water, the vanadium (IV) oxidises the iodide to iodine instantaneously. Complexes of the type $VOX_2.2L$ where $X = Cl^-$ and Br^- and L = HMPA or TMU also been prepared and studied.

All the compounds prepared, with the exception of the iodide, were soluble in polar organic solvents e.g. nitromethane, methyl cyanide etc. and insoluble in non-polar organic solvents. The compounds are all hygroscopic; $VOCl_2.2.5CH_3CN$ being very much so.

Experimental Section

The hygroscopic compounds were handled in a dry-box. Ultraviolet and visible spectra were determined with a Beckman DK2A ratio recording spectrophotometer. Infrared spectra were determined with a Unicam SP200 G recording spectrophotometer using smears for the free ligands and nujol mulls (in the case of the nitratocomplex also hexachlorobutadiene mulls) of the solids between rock salt plates. Conductivity measurements were made with an Industrial Instrument Inc. Model RC 16B2 conductivity bridge.

Materials. The nitromethane for conductivity measurements was left for twelve hours—over The other solvents were dried and purified by published methods.[6]

The preparation of anhydrous vanadyl chloride was described in the previous section. Analysis indicated a vanadium to chloride ratio of 1 : 1.96. (Found: V, 32.8; Cl, 45.0. Calc. for $VOCl_2$: V, 36.93; Cl, 51.48%). By using this vanadyl chloride very pure $VOCl_2.2.5CH_3CN$ was prepared. (See the following paragraph). Further purification of the anhydrous vanadyl chloride was unnecessary.

Preparation of the complexes. Each of the complexes was prepared at least twice and analysed twice.

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(1) J. Selbin, *Chem. Rev.*, 65, 153 (1965); 1(a) *ibid.*, 156; 1(b) *ibid.*, 157.

(2) G. Brauer, «Handbuch der Preparativen An-organischen Chemie», F. Encke, Stuttgart (1962).

(3) H. Funk and W. Z. Weiss, *Anorg. Allgem. Chem.*, *295*, 327 (1958).

(4) H. E. Roscoe, *J. Chem. Soc.*, *21*, 322 (1868); *23*, 344 (1870); *24*, 23 (1871).

(5) P. A. Kitty and D. Nicholls, *J. Chem. Soc.*, 4915 (1965).

(6) J. G. H. du Preez and F. G. Sadie, *J.S.A. Chem. Inst.*, *XIX*, 73 (1966).

Except $VOCl_2 . 2.5CH_3CN$ and $VO(DMSO)_5I_2$ the complexes were recrystallised once from either nitromethane or methyl cyanide.

$VOCl_2 . 2.5CH_3CN$-Anhydrous vanadyl dichloride (~2 g) was dissolved in pure dry acetonitrile (10 ml). A dark blue hot solution was formed as a result of the exothermic reaction. Some yellow insoluble material (impurities in the vanadyl chloride) was filtered off and the solution cooled. Dark bluc crystals of $VOCl_2 . 2.5CH_3CN$ were slowly deposited. These were vacuum dried and analysed.

Dinitrato-bis-(hexamethylphosphoramide) oxovanadium(IV). To a concentrated solution of $VOCl_2 . 2.5CH_3CN$ in methyl cyanide was added excess HMPA. The blue colour of the solution changed to a blue-green. The stoichiometric amount of a concentrated acetonitrile solution of silver nitrate was now added. Silver chloride precipitated, the supernatant solution turned dark blue again. After filtration and concentration blue crystals of $VO(NO_3)_2 . 2HMPA$ formed. These were vacuum dried and analysed.

Efforts to prepare other nitrate-or nitrato-complexes with DMSO, TMU and CH_3CN as ligands, failed. Soon after the silver nitrate was added a yellow-brown product containing vanadium(V) precipitated in each case, due to oxidation by the nitrate.

Pentakis(dimethylsulphoxide)oxovanadium(IV)iodide. To $VOCl_2 . 2TMU$ (1.22 g) dissolved in anhydrous methyl cyanide (20 ml) was added N,N,N′,N′-tetramethylurea (2 ml) and a 15% solution of anhydrous sodium iodide in methyl cyanide (7.5 ml). A white precipitate of sodium chloride formed. After centrifugation and decantation anhydrous ether was added to the blue-green solution. The blue-green oil which separated was dissolved in pure methylene dichloride when the excess sodium iodide precipitated. To the supernatant was added isopentane when a blue-green oil separated. This was washed with ethyl acetate and ether. After dissolution in methyl cyanide pure dimethylsulphoxide was added. A blue-green crystalline precipitate of $VOI_2 . 5DMSO$ formed immediately. This was washed with ether and vacuum dried. Efforts to isolate iodide-complexes of HMPA and TMU failed since iodine was evolved upon concentration.

$VOX_2 . 2L$ ($X = Br^-$ or Cl^- complexes were all prepared by refluxing concentrated aqueous solutions of VOX_2 in the presence of excess HX and excess ligand with 2,2-dimethoxypropane and acetone. Crystallisation took place either upon cooling in a salt-ice mixture or by addition of ethyl acetate before cooling. The precipitates were finally washed with ethyl acetate and isopentane before vacuum drying. Efforts to isolate solid complexes of $VOCl_2$ and $VOBr_2$ with N,N-dimethylacetamide and N,N-dimethylformamide failed, as blue oils were obtained in each case.

Analysis. Vanadium was determined complexometrically[7] except in the nitrato and the iodide-complexes. The nitrato-complex was dissolved in excess dilute aqueous $KMnO_4$. The excess $KMnO_4$ was removed by H_2O_2.

The nitrate was then determined gravimetrically with nitron[8] and the vanadium determined spectrophotometrically by using 30% H_2O_2.[9]

The iodide-complex was dissolved in N,N-dimethylacetamide and a methyl cyanide solution of silver nitrate was added. The silver iodide was then coagulated in boiling 0.05 N nitric acid and determined gravimetrically. The vanadium determination was similar to that used for the nitrato-complex.

Results and Discussion

The molar conductivities of the complexes in nitromethane (Table I) indicate that little ionisation takes place, except perhaps in the case of the nitrato-complex.

Table I. Molar conductivities in nitromethane

Compound	Λ_{500} (mho cm^2)	Λ_{1000} (mho cm^2)
$VOCl_2 . 2$ HMPA	17.6	17.8
$VOBr_2 . 2$ HMPA	27.8	32.5
$VO(NO_3)_2 . 2$ HMPA	66.4	99.3
$VOCl_2 . 2$ TMU	16.0	17.0
$VOBr_2 . 2$ TMU	20.7	24.8

The Λ_{1000}-value of this complex [$VO(NO_3)_2 . 2HMPA$] corresponds with a 1:1 electrolyte although the great difference (32.9 mho cm^2) between the Λ_{500}-value and the Λ_{1000}-value indicates that nitrate is gradually replaced by solvent upon dilution. The increase in the Λ_{1000}-values for the hexamethylphosphoramide complexes in the direction chloro, bromo to nitrato indicates that the donor properties towards oxovanadium(IV) also decrease in the same sequence.

The infrared spectra of the free ligands and the complexes were determined in the region 650 cm^{-1} to 1600 cm^{-1}. The position of the $E=O$ ($E=P$, S and C) stretching vibrations in the complexes (Table IIa) differs greatly from those in the free ligands (Table IIb)

Table II.(a) Infrared spectral and analytical data of oxovanadium(IV) complexes

Compound	$\Delta E=0$ cm^{-1} ($E=P$, S or C)	% Vanadium Found	% Vanadium Calc.	% Cl^-, Br^-, I^- or NO_3^- Found	% Cl^-, Br^-, I^- or NO_3^- Calc.
$VOCl_2.2HMPA$	80	10.30	10.26	14.39	14.31
$VOBr_2 2HMPA$	88	8.68	8.70	27.24	27.32
$VO(NO_3)_2.2HMPA$	95	9.24	9.27	22.53	22.57
$VOCl_2.2TMU$	62	13.74	13.77	19.22	19.19
$VOBr_2.2TMU$	70	11.0	11.1	34.91	34.85
$VOI_2.5DMSO$	80	7.21	7.17	35.65	35.70
$VOCl_2.2.5CH_3CN$	—	21.3	21.2	29.44	29.50

Table II.(b)

Ligand	ν $E=O$
HMPA	1220 cm^{-1}
TMU	1650 cm^{-1}
DMSO	1045 cm^{-1}

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(7) F. J. Welcher, «Analytical uses of E.D.T.A.», Van Nostrand, p. 205 (1958).

(8) A. I. Vogel, «A Textbook of Quantitative Inorganic Analysis», 3rd edn., Longmans, London (1963).

(9) S. M. Horner, S. Y. Tyree and D. L. Venezky, *Inorg. Chem.*, *1*, 844 (1962).

and are comparable to those published for similar compounds.[9] The shifts in the phosphoryl and carbonyl stretching frequencies for the HMPA and TMU-complexes of $VOBr_2$ are bigger than those of the corresponding $VOCl_2$ complexes. The greater reduction in the π-bond order of the E=O (E=Pand C) in the ligand suggests a greater interaction between vanadium and ligand oxygens in the bromo-complex. The infrared spectra of the nujol and hexachlorobutadiene mulls of the nitrato-complex gave symmetric and asymmetric stretching vibrations at about 1350 cm^{-1} and 1500 cm^{-1} respectively; these are typical of a covalent nitrate[10] group. This observation thus provides supporting evidence, independently of the conductivity data, that the nitrato-group is coordinated to the vanadium.

The V=O stretching frequency in the chloro- and bromo-complexes of TMU were found to lie at 995 and 992 cm^{-1} respectively. In the case of the HMPA- and DMSO-complexes this frequency is masked by ligand frequencies.

The ultraviolet and visible spectral data of the complexes (Table III) resemble data published[11] for comparable compounds. In most cases the three ligand field bands were observed in these spectra.

Table III. Visible and Ultraviolet Band Maxima (in kK = 1000 cm^{-1} units) for oxovanadium(IV) complexes

Compound	Band	Solid reflectance spectrum	Nitromethane solution (~ 0.015M)	Methylene dichloride (solution (~ 0.015M)
$VOCl_2 . 2$ HMPA	I	(sh)?***	11.8 (sh)**	11.9 (sh)
	II	13.40	13.8 (33)*	13.6 (31)
	III	25.60 (sh)	25.6	25.6
$VOCl_2 . 2$ TMU	I	(sh)?	12.9 (sh)	12.9 (sh)
	II	15.2	15.0 (43)	15.0 (42)
	III	—	25.0	24.5
$VOBr_2 . 2$ HMPA	I	(sh)?	11.6 (sh)	11.6 (sh)
	II	13.8	13.7 (35)	13.9 (42)
	III	—	26.0	25.3
$VOBr_2 . 2$ TMU	I	(sh)?	(sh)?	12.5 (sh)
	II	15.4	15.5 (43)	15.2 (44)
	III	—	26.1	24.4
$VOI_2 . 5$ DMSO	I	12.7		
	II	15.4 (sh)		
	III	—		
$VO(NO_3)_2 . 2$ HMPA	I	13.0		
	II	15.0 (sh)		
	III	—		

* Indicates molar extinction coefficient of most prominent band. ** (sh) indicates prominent shoulder. *** (sh)? indicates the possibility of a shoulder but difficult to determine position.

Only in a few instances was the third band obscured by charge transfer spectra. The solid reflectance spectrum of the iodide complex closely resembles the published spectrum[11] of a methyl cyanide solution of $VOBr_2 . 5DMSO$ namely, band I at 12.9 kK and band II at 15.5 kK. Band III of the iodide was obscured by charge transfer peaks. In both cases the vanadium is probably surrounded by six oxygens: the vanadyl oxygen, and five DMSO oxygens in a tetragonally distorted octahedron. Furthermore, it would appear that the chloro- and bromo-complexes are unionised and five coordinated in non-aqueous solution. This follows from the fact that the spectra in nitromethane and methylene dichloride solutions are very similar to those of the solid reflectance spectra. Similar symmetries and ligand fields would account for these observations.

Although it may be argued[9] that such five coordinated complexes would result in molecular energy level diagrammes not greatly different from those of the distorted six coordinated species, we observed slightly greater differences between the spectra of these two species. In each of the chloro- and bromo-complexes (Table III) the second ligand field band was found to be the more intense one, so that band I was found as a shoulder on band II whereas for the six coordinated species it was vice versa.

The spectrum of the nitrato-complex was sligthly different in so far as the intensity of bands I and II differed very little, with the first band slightly more intense. Although the characterisation of this compound indicated covalent nitrate groups, the symmetry of the complex is not known. If one nitrate group acts as a bidentate ligand the complex can be six coordinated.

According to the molecular orbital model of Ballhausen and Gray[12] for $VO(H_2O)_5^{++}$ the assignments for band I is $^2B_2 \rightarrow {}^2E(1)$, band II $^2B_2 \rightarrow {}^2B_1$ and band III $^2B_2 \rightarrow {}^2A_1$. The value for 10 Dq determined according to this scheme is that of band II. This would mean that the ligand field strength of TMU is bigger than HMPA for VO^{++}. The positions of the second ligand field bands in the chloro- and bromo-complexes of TMU and HMPA respectively seems to indicate that bromide has a greater ligand field than chloride for VO^{++} in these cases. Although somewhat surprising, it can possibly be explained by the relatively greater interaction between the oxovanadium(IV) ion and the phosphoryl (carbonyl) oxygen of the ligand as indicated by the infrared spectra. A crystal structure analysis of $VOCl_2 . 2HMPA$ and $VOBr_2 . 2HMPA$ has been undertaken in this laboratory.

A similar analysis is envisaged for $VOCl_2 . 2.5CH_3CN$.

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[10] K. W. Bagnall, D. Brown and J. G. H. du Preez, *J. Chem. Soc.*, 5523 (1964).

[11] J. Selbin, *Chem. Rev.*, *65*, 166 (1965).

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