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Ethanolates and Heterocyclic Amine Complexes of Vanadium(II)

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New vanadium(II) alcoholates, $VBr_2 \cdot 6EtOH$, $VCl_2 \cdot 4EtOH$ and $VCl_2 \cdot 2EtOH$ have been prepared and used with hydrated vanadium(II) salts for the synthesis of vanadium(II) heterocyclic amine complexes. Magnetic and reflectance spectra data show that complexes formulated as $[VL_4X_2]$, where L = a heterocyclic amine, have a distorted octahedral structure whereas complexes of the type $[VL_6]X_2$ have octahedral geometry (X = Cl, Br and I). The amines used in this work were pyrazole (pz), imidazole (iz), 2-methylimidazole (2-miz), benzimidazole (biz) and isoquinoline (iq).

Introduction

Vanadium(II) halide methanolates have been made by the electrolysis of anhydrous vanadium(III) chloride in methanol under argon [1]. By careful heating of the hexasolvated vanadium(II) complexes the tetrakis- and bis-methanolates were formed.

The first part of this paper describes an alternative route for vanadium(II) alcoholate synthesis involving the treatment of ethanolic solutions of hydrated vanadium(II) salts with the organic ester, triethylorthoformate. The compounds $VBr_2 \cdot 6EtOH$, $VCl_2 \cdot 4EtOH$ and $VCl_2 \cdot 2EtOH$ thus obtained have been found to have distorted octahedral structures, the last through chloride bridges. The compound $VI_2 \cdot 6MeOH$ is known to have octahedral stereochemistry [1] and it has now been prepared by treating $VCl_2 \cdot 4EtOH$ or $VCl_2 \cdot 2EtOH$ with KI in methanol. The vanadium(II) alcoholates were made because of their potential use for the prepararation in non-aqueous solvents of vanadium(II) complexes with weak donor ligands, or complexes which might be oxidised by water.

The second part of this paper reports the preparation and properties of the complexes (a) $[V(amine)_4X_2]$ in which the amine is pyrazole (X = Cl, Br and I), 2-methylimidazole (X = Cl), and isoquinoline (X = Cl, Br and I), and (b) $[V(amine)_6]X_2$ where the amine is imidazole (X = Cl, Br and I) and 2-methylimidazole (X = Br and I). Reactions of vanadium(II) alcoholates with ethanolic solutions of benzimidazole gave rise to products of approximate composition $[V(amine)_4X_2] \cdot 2EtOH$ where X = Br and I. Some of the complexes were reported [3] during our investigations [4], and, in addition, a number of vanadium(II) complexes of the related ligands N-methylimidazole and 1,2-dimethylimidazole were prepared [3b]. A series of complexes of composition $[VL_4X_2]$ where L = pyridine or a substituted pyridine; X = Cl, Br, I [5] and NCS [6] are also known as well as $[V(\beta\text{-picoline})_2Br_2]$ and $[V(\gamma\text{-picoline})_2Br_2]$, which exhibit [5] strong antiferromagnetism indicative of a polymeric bromide-bridged structure, and some vanadium(II) complexes of ethylenediamine and related ligands.

Experimental

The method of preparation of $VBr_2 \cdot 6EtOH$ and $VCl_2 \cdot 4EtOH$ was to dissolve the corresponding hydrates [7a] in ethanol, to which an excess of triethylorthoformate was added. Evaporation to dryness (to small volume with the bromide) of the turquoise solution gave a mixture of the vanadium(II) alcoholate and ethyl formate, the ester having reacted with the water of hydration [8] in the vanadium(II) salt. The solid was shaken with two portions of sodium-dried ether to extract the ethyl formate, and the vanadium(II) salt was filtered off, washed with ether or an ether/ethanol mixture, and dried under continuous pumping. Traces of a green substance, probably $VCl_2 \cdot 2EtOH$, were seen among the blue crystals of $VCl_2 \cdot 4EtOH$ and may be responsible for the low carbon analyses (Table I).

To prepare $VCl_2 \cdot 2EtOH$, the dihydrate $VCl_2 \cdot 2H_2O$ was dissolved in a mixture of equal parts of ethanol and triethylorthoformate. The solvent was removed at 50–60 °C under vacuum to leave a pale green powder containing ethyl formate which was extracted with sodium-dried ether. After filtration

TABLE I. Analyses and Magnetic Data of Vanadium(II) Alcoholates.

Complex	Colour	C[a]	H	V	T/K	μ_{eff}[b]/BM	θ[b]/°	$10^6 \times$ Diamagnetic Correction/cm^3 mol^{-1}
$VBr_2 \cdot 6EtOH$	lilac	27.5(29.6)	7.2(7.5)	11.2(10.6)	295	3.80	0	266
					90	3.78		
$VI_2 \cdot 6MeOH$	red-violet	13.3(14.5)	4.6(4.9)	10.0(10.3)	295	3.82	0	223
					90	3.81		
$VCl_2 \cdot 2EtOH$	pale green	19.1(22.5)	5.5(5.7)	25.0(23.8)	295	3.33	113	99
					90	2.61		
$VCl_2 \cdot 4EtOH$	pale blue	28.5(31.4)	7.5(7.9)	17.2(16.6)	295	3.68	8	177
					90	3.56		

[a] Calculated percentages in parentheses. [b] Calculated from $\mu_{eff} = 2.828 (\chi_A T)^{1/2}$ and the Curie-Weiss law $\chi_A^{-1} \alpha (T + \theta)$.

TABLE II. Analyses and Magnetic Data of Vanadium(II)-Heterocyclic Amine Complexes.

Complex	Colour	C[a]	H	N	V	T/K	μ_{eff}[b]/BM	$10^6 \times$ Diamagnetic Correction/cm^3 mol^{-1}
$[V(pz)_4Cl_2]$	blue-green	36.2(36.5)	4.2(4.1)	27.9(28.4)	12.7(12.9)	295	3.71	277
						90	3.72	
$[V(pz)_4Br_2]$	blue-green	29.6(29.8)	3.4(3.3)	22.9(23.2)	10.2(10.5)	295	3.82	192
						90	3.80	
$[V(pz)_6]I_2$	green	30.7(30.3)	3.6(3.4)	22.1(23.6)	6.9(7.1)	295	3.78	286
						90	3.86	
$[V(iz)_6]Cl_2$	green	40.5(40.8)	4.6(4.6)	31.5(31.7)	9.3(9.6)	295	3.77	171
						90	3.80	
$[V(iz)_6]Br_2$	green	35.1(34.9)	3.9(3.9)	26.5(27.1)	8.3(8.2)	295	3.75	258
						90	3.79	
$[V(iz)_6]I_2$	green	30.1(30.3)	3.4(3.4)	23.7(23.6)	6.9(7.1)	295	3.77	286
						90	3.78	
$[V(2miz)_4Cl_2]$	lilac	42.4(42.7)	5.9(5.4)	24.1(24.9)	11.0(11.3)	295	3.62	223
						90	3.62	
$[V(2miz)_6]Br_2$	pink	40.4(41.0)	5.2(5.2)	23.3(24.0)	7.3(7.3)	295	3.84	335
						90	3.87	
$[V(2miz)_6]I_2$	pink	35.6(36.1)	4.5(4.6)	19.8(21.1)	6.3(6.4)	295	3.80	363
						90	3.82	
$[V(biz)_4Br_2] \cdot 2EtOH$	yellow-green	49.2(49.6)	4.0(4.7)	15.7(14.5)	6.9(6.5)	295	3.66	349
						90	3.65	
$[V(biz)_4I_2] \cdot 2EtOH$	yellow	43.3(44.2)	4.1(5.0)	13.1(12.9)	6.0(5.8)	295	3.58	377
						90	3.49	
$[V(iq)_4Cl_2]$	royal blue	66.4(67.7)	4.4(4.4)	8.4(8.8)	8.1(8.0)	295	3.69	273
						90	3.68	
$[V(iq)_4Br_2]$	royal blue	60.1(59.4)	3.9(3.9)	7.8(7.7)	6.9(7.0)	295	3.71	294
						90	3.72	
$[V(iq)_4I_2]$	blue	52.2(52.6)	3.4(3.4)	6.7(6.8)	6.2(6.2)	295	3.76	322
						90	3.78	

[a] Calculated values in parentheses. [b] The Weiss constant θ was approximately 0° for all these complexes.

and washing with ether the $VCl_2 \cdot 2EtOH$ was vacuum dried.

The alcoholate $VI_2 \cdot 6MeOH$ was prepared by treating a methanolic solution of $VCl_2 \cdot 4EtOH$ or $VCl_2 \cdot 2EtOH$ with a methanolic solution of KI. Precipitated KCl was filtered off, and the filtrate evaporated to dryness, to give a fluffy, red-violet solid which was washed with sodium-dried ether before drying under vacuum. Each of the vanadium(II) alcoholates oxidised very rapidly when exposed to the air. This presented considerable difficulty in the accurate determination of the C, H and N content of the vanadium(II) alcoholates for which the results are poor. However generally good analytical data were obtained for the complexes (Table II) prepared from the alcoholates and various heterocyclic amines in ethanol or diethyl ether/absolute ethanol mixtures. Complexes of the type $[V(iz)_6]X_2$, where X = Cl, Br and I, were precipitated from solutions containing a ligand-to-metal ratio of 6:1. Reactions of pyrazole with $VBr_2 \cdot 6H_2O$ and $VCl_2 \cdot 4H_2O$ gave tetrakis(pyrazole) complexes even when ligand-to-metal ratios exceeded 6:1. Attempts to prepare the iodide $[V(pz)_4I_2]$ from $VI_2 \cdot 6MeOH$ and pyrazole were unsuccessful; instead $[V(pz)_6]I_2$ was obtained. Treatment of vanadium(II) hydrated salts with 2-methylimidazole (1:6 molar ratio) produced the hexakis-substituted species, except in the case of chloride when $[V(2miz)_4Cl_2]$ was formed. The complexes $[V(iq)_4X_2]$, where X = Cl, Br and I, were isolated from solutions containing either 4:1 or 6:1 ligand-to-metal ratios. Attempts to prepare complexes of quinoline and benzotriazole were unsuccessful. Some reactions were carried out in which vanadium(II) halides were treated with benzimidazole (1:4 molar ratio). Yellow-green crystalline products that analysed reasonably well for $[V(biz)_4X_2] \cdot 2EtOH$ were obtained where X = Br and I. Attempts to prepare hexakis(benzimidazole) complexes were unsuccessful. Similar reactions using $VCl_2 \cdot 2H_2O$ gave products with poor analyses for the formulation $[V(biz)_4Cl_2] \cdot 2EtOH$ and whose composition was uncertain.

The complexes (0.1 to 0.3 g) were analysed for vanadium by heating to dryness with a few drops of concentrated sulphuric and nitric acids and digesting the residue for several hours with concentrated sulphuric acid (1 cm^3) and 75% perchloric acid (30 cm^3). The solution containing vanadium(V) was diluted with water (70 cm^3) and treated with syrupy phosphoric acid (15 cm^3). Excess of 0.05 *N* ferrous ammonium sulphate was added and back titrated with 0.05 *N* potassium permanganate using ferroin indicator.

Magnetic susceptibility measurements were carried out by the Gouy method over a temperature range 90–295 K, and the field was calibrated with $Hg[Co(NCS)_4]$. Diffuse reflectance and solution spectra were recorded over the range 45000 to 5000 cm^{-1} on a Unicam SP700C spectrophotometer.Cells containing lithium fluoride or pure solvent were used as references where appropriate.

Results and Discussion

The magnetic data for $VBr_2 \cdot 6EtOH$ and $VI_2 \cdot 6MeOH$ (Table I) are consistent with an octahedral arrangement of alcohol ligands bound to the vanadium(II) ion. Both compounds obey the Curie law having temperature-independent magnetic moments as expected slightly below the spin-only value of 3.87 B.M. for the $3d^3$ configuration. Smaller temperature-variable moments were recorded for the complex $VCl_2 \cdot 2EtOH$ (3.33 and 2.61 B.M. respectively at room and liquid nitrogen temperatures) which has a large Weiss constant of 113°. This is attributed to antiferromagnetic exchange interactions arising from a chloride-bridged polymeric structure. Distortion from octahedral symmetry in $VCl_2 \cdot 4EtOH$ is suggested by its lower moments at room and liquid nitrogen temperatures, 3.68 and 3.56 B.M. respectively. Generally similar magnetic behaviour was observed with the methanol adducts [1]. Effective magnetic moments, a little below the spin-only value and independent of temperature, confirmed the oxidation state in the magnetically-dilute vanadium(II) heterocyclic amine complexes (Table II). Similar magnetic moments at room temperature for some of these compounds have already been reported [3].

The solution spectrum of $VBr_2 \cdot 6H_2O$ in ethanol was monitored as a function of triethylorthoformate added to check that no oxidation occurred during the dehydration. Increasing the ester concentration slightly reduced the ν_1 and ν_2 band intensities (Table III) corresponding to the transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$, and although the solution turned from lilac to turquoise, bands characteristic of vanadium(III) alcoholates [9] were not present. Any variation in the third band $\nu_3\{{}^4A_{2g} \rightarrow {}^4T_{1g}(P)\}$ was not investigated. In an ethanol/triethylorthoformate medium $VBr_2 \cdot 6EtOH$ was readily formed. Redissolved in ethanol, the $VBr_2 \cdot 6EtOH$ solution spectrum has bands at 26000 cm^{-1}, 17000 cm^{-1} ($\epsilon \sim 6$ dm^3 mol^{-1} cm^{-1}) and 11200 cm^{-1} ($\epsilon \sim 4$ dm^3 mol^{-1} cm^{-1}), *i.e.* a typical vanadium(II) spectrum.

Diffuse reflectance spectral data for $VBr_2 \cdot 6EtOH$ and $VI_2 \cdot 6MeOH$ are consistent with an octahedral microsymmetry about the vanadium(II) ion. The electron repulsion parameters (Table III) were deduced from the diagonal sum rule [10] ($15B' = \nu_2 + \nu_3 - 3\nu_1$) or from the appropriate secular determinant [11]. Evidence of distortion from octahedral symmetry is present in the spectrum of $VCl_2 \cdot 4EtOH$ which accords well with the magnetic data for this complex. The ν_1 band is split into two components at 12400 and 9800 cm^{-1}. These are respectively assigned to the transitions ${}^4B_{1g} \rightarrow {}^4B_{2g}$and ${}^4B_{1g} \rightarrow {}^4E_g{}^a$ in a weak axial field. The ν_2 band also appears to be split. Similar results obtain for $VCl_2 \cdot 4H_2O$ [7b]. The strong axial field in polymeric $VCl_2 \cdot 2EtOH$ due to the ethanol ligands establishes the order ${}^4B_{2g} < {}^4E_g{}^a < {}^4E_g{}^b < {}^4A_{2g}$, and interaction between the E_g levels tends to reduce the band splitting. The ν_1 band in $VCl_2 \cdot 2EtOH$ is slightly split but ν_2 appears symmetrical in the room temperature spectrum. At liquid nitrogen temperature the

TABLE III. Reflectance and Solution Spectra of Vanadium(II) Alcoholates.

Compound	T/K	Band Max ($10^{-3}\nu$/cm^{-1})							Dq	Electron Repulsion Parameters		Calc. Band Positions		
		ν_3		ν_2			ν_1			B′	β^a	ν_3	ν_2	ν_2/ν_1
$VBr_2 \cdot 6EtOH$	295	27.0		16.9			12.0		1.20	0.493	0.644	26.5	16.9	1.41
	90	25.5		17.2			12.1							
solution[b]		26.0		17.0		12.2[c]	11.2		1.12	0.660	0.862	26.6		1.41
$VBr_2 \cdot 6H_2O$	295	30.0		17.6			11.7		1.17	0.659	0.860	32.0		1.50
	90	30.0		18.1			12.2							
solution[b]		27.9		17.4			11.55		1.16	0.660	0.862	27.1		1.51
$VI_2 \cdot 6MeOH$	295	28.4		17.7			12.0		1.20	0.673	0.873	28.1	18.0	1.48
	90	28.5		17.8			12.3							
				ν_2			ν_1							
$VCl_2 \cdot EtOH$	295	24.2		14.2		9.3		8.6	0.93	0.566[d]	0.739	22.2		1.53
	90	24.4	15.0		13.8	10.1		9.5						
$VCl_2 \cdot 4EtOH$	295	25.1	17.2		16.4	12.4		9.8	0.98	0.806[e]	0.950	25.7	15.8	1.67
	90	25.0	17.3		15.8	12.0		10.0						

[a] β = B′/B where B is the free-ion value for V^{2+} (766 cm^{-1}). [b] Recorded in ethanol. [c] Weak shoulder on ν_1. [d] Calculated by assuming ν_1 = 9300 cm^{-1}. [e] Calculated by assuming ν_1 = 9800 cm^{-1} and ν_2 = 16400 cm^{-1}.

TABLE IV. Reflectance Spectra of Vanadium(II)–Heterocyclic Amine Complexes.

Compound	T/K	Band Max ($10^{-3}\nu$/cm^{-1})						Dq	Electron Repulsion Parameters		Calc. Band Positions	
		ν_2			ν_1							
									B′	β	ν_3	ν_2/ν_1
$V(pz)_4Cl_2$	295	20.2		16.25	15.8		11.6	1.58	0.406[a]	0.530	34.53	1.29
	90	21.0		16.6	15.8		11.6					
$V(pz)_4Br_2$	295	20.1			15.25		10.45	1.53	0.454[b]	0.593	32.57	1.82
	90	20.45			15.35		10.6					
$[V(pz)_6]I_2$	295		23.0			16.0		1.60	0.722	0.943	35.84	1.44
	90		23.4			16.4						
$[V(iz)_6]Cl_2$	295		23.0			16.0		1.60	0.722	0.943	35.84	1.44
	90		23.2			16.5						
$[V(iz)_6]Br_2$	295		23.0			16.0		1.60	0.722	0.943	35.84	1.44
	90		23.6			16.25						
$[V(iz)_6]I_2$	295		22.6			15.7		1.57	0.715	0.933	35.23	1.44
	90		23.0			16.05						
$[V(2miz)_4Cl_2]$	295		15.0			9.4		0.94	0.440[c]	0.574	–	1.60
	90	15.2		13.0	11.4		9.8					
$[V(2miz)_6]Br_2$	295		20.2			13.7		1.37	0.703	0.918	31.42	1.47
	90		20.65			14.0						
$[V(2miz)_6]I_2$	295		20.0			13.65		1.37	0.677	0.884	31.10	1.47
	90		20.4			14.0						

[a] Calculated by assuming ν_1 = 15800 cm^{-1} and ν_2 = 20200 cm^{-1}. [b] Calculated by assuming ν_1 = 15250 cm^{-1} and ν_2 = 20100 cm^{-1}. [c] Calculated by assuming ν_1 = 9400 cm^{-1} and ν_2 = 15000 cm^{-1}.

band energies generally moved to somewhat higher wavenumber as expected for spin-allowed transitions, and some splitting of ν_2 became apparent for $VCl_2 \cdot 2EtOH$.

The spectrum (Table IV) of $[V(pz)_4Cl_2]$ indicates that ν_1 is split into two components at 15800 and 11600 cm^{-1}. These are assigned to the transitions $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4B_{1g} \rightarrow {}^4E_g{}^a$ respectively. The absorptions at 20200 and 16250 cm^{-1} may be due to splitting of ν_2. It is possible that in the bromide $[V(pz)_4Br_2]$ the strong band at 15250 cm^{-1} contains a superimposition of split components from ν_1 and ν_2, the weak band at 10450 cm^{-1} being the $^4B_{1g} \rightarrow {}^4E_g{}^a$ component of ν_1. Overlapping of components from ν_1 and ν_2 in the spectrum of the bromide and not the chloride also occurred with $VBr_2 \cdot 4H_2O$ and $VCl_2 \cdot 4H_2O$ [7b]. The distortion from octahedral symmetry also shows itself in the low values of B′ for $[V(pz)_4Cl_2]$ and $[V(pz)_4Br_2]$.

The complex $[V(pz)_6]I_2$ has a shoulder at 23000 cm^{-1} due to ν_2, a band at 16000 cm^{-1} arising from ν_1, and a reasonable value of B′ (722 cm^{-1}) has been calculated, confirming its octahedral structure. The remaining hexakis (amine) complexes also exhibit the spectra expected for octahedral vanadium(II). The room temperature spectrum of $[V(2miz)_4Cl_2]$ contains broad bands at 9400 and 15000 cm^{-1}, but these split at liquid nitrogen temperature, and B′ is low suggesting distortion as would be expected through coordination of chloride.

Only one band is clearly discernable in the reflectance spectra of the vanadium(II)–benzimidazole complexes. This occurs at 14500 cm^{-1} for the bromide and 14300 cm^{-1} for the iodide. Broad and intense asymmetrical bands, unlike those found in the pyrazole complexes, appear in the spectra of tetrakis(isoquinoline)vanadium(II) halides. These are not amenable to simple interpretation and resemble those found in vanadium(II) compounds containing 8-aminoquinoline [12, 13].

X-ray powder photographs showed that the hexakis(imidazole) complexes are isomorphous, but there were no such relationships among the other complexes.

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