Vanadium(II) Complexes of Substituted Imidazoles

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The preparation and properties of new hexaco-ordinate vanadium(II) complexes with the ligands N-methylimidazole (Nmiz), 1,2-dimethylimidazole (dmiz), and benzimidazole (benziz) are reported. The complexes have the formulae $[VL_6]X_2$ *(L = Nmiz, X = I, BPh_4),* $[VL_6]X_2 \cdot 2C_4H_9OH$ *(L = Nmiz, X = Cl, Br), and* $[VL_4X_2]$ *(L = Nmiz, X = NCS; L = dmiz, X = Cl, Br, NCS; L = benziz, X = Br). The compound* $[V(benziz)_2Cl_2] \cdot 0.5C_4H_9OH$ *has been also obtained. Heating of* $[V(Nmiz)_6]X_2 \cdot 2C_4H_9OH$ *yields compounds of stoichiometry* $V(Nmiz)_4Cl_2$ *and* $V(Nmiz)_5Br_2$. *The coordination geometry of the reported complexes is proposed on the basis of spectral and magnetic data.*

Introduction

Up to date the number of complexes of vanadium-(II) known is small, probably due to the poor acceptor ability of this ion; besides their properties have been little investigated owing to the high sensitivity of vanadium(II) to oxidation by air and water.

As a matter of fact the coordination chemistry of vanadium(II) has been confined to the hydrated salts and some halides [1], and recently to complexes with some nitrogen containing ligands on which only preliminary accounts have been so far reported [2].

We reporte here the preparation and characterization of vanadium(II) complexes with the ligands N-methylimidazole (Nmiz, I), 1,2-dimethylimidazole (dmiz, II), and benzimidazole (benziz, III).

I II III
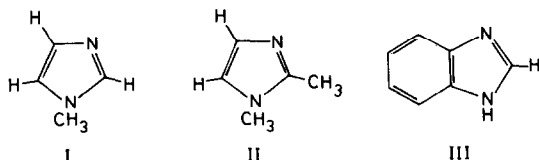
Experimental

N-methylimidazole, 1,2-dimethylimidazole, and benzimidazole are available from Fluka A.G. and were employed without further purification.

Hydrated vanadium(II) halides were prepared by the electrolytic reduction of acid solutions of the appropriate vanadyl(IV) halides with a mercury cathode [3], and by subsequent evaporation to dryness of the solutions at 60–70 °C at reduced pressure. The hydrated vanadium(II) halides were dissolved in CH_3OH or C_2H_5OH, evaporated to dryness several times, and finally heated at 100 °C under vacuum.

All complexes were prepared under dry nitrogen, using n-butanol as solvent unless otherwise stated.

$V(Nmiz)_6X_2$ (X = I, BPh_4)

The complexes were obtained by mixing warm solutions of the reactants and gently heating. The tetraphenylborate derivative readily formed upon adding a solution of sodium tetraphenylborate.

$V(Nmiz)_6X_2 \cdot 2C_4H_9OH$ (X = Cl, Br)

These complexes were obtained by leaving dilute solutions of the reactants – the ligand being in excess to the stoichiometric ratio – to stand for one or two days at room temperature.

$V(Nmiz)_4Cl_2$ and $V(Nmiz)_5Br_2$

These have been obtained by heating the parent hexakis derivatives to constant weight at 80–100 °C under vacuum. These complexes, dissolved in a solution of the ligand, yielded the hexakis derivatives on standing.

$V(dmiz)_4X_2$ (X = Cl, Br)

A boiling solution of vanadium(II) halide was added to a boiling solution of the ligand in o-dichlorobenzene in excess to the stoichiometric ratio. The resulting solutions were concentrated by heating until crystals separated from the mixture.

$VL_4(NCS)_2$ (L = Nmiz, dmiz)

To a warm solution of vanadium(II) chloride and the appropriate ligand, a warm solution of sodium thiocyanate dissolved in ethanol was added. The mixture was filtered to eliminate sodium chloride and evaporated until crystals formed.

V(benziz)₂Cl₂·0.5C₄H₉OH

V(benziz)₂Cl₂·0.5C₄H₉OH

To a solution of vanadium(II) chloride in excess to the stoichiometric ratio and benzimidazole, di-n-buthyl ether was added and the resulting solution heated to boiling temperature until a green product separated.

V(benziz)₄Br₂

To a solution containing vanadium(II) bromide and the ligand in excess to the stoichiometric ratio, di-n-buthyl ether was added and the resulting solution evaporated until a brown oil formed. This oil was separated from the solution, dissolved in the minimum amount of n-butanol and finally the solution was heated until a solid product formed.

In all these preparations the solid products formed from the solutions were washed by decantation with a mixture of n-butanol and petroleum ether (or n-butanol with di-n-butyl ether), filtered, washed with petroleum ether alone, and finally dried off by standing in a stream of dry nitrogen at 100 °C. The V(Nmiz)₆X₂·2C₄H₉OH derivatives were dried at room temperature to avoid loss of the ligand.

The analytical data are reported in Table I.

Magnetic and spectrophotometric measurements have been performed with the apparatus already described [4], on samples contained in suitable airtight containers (Gouy tube and uv cells) filled in dry-box under inert atmosphere.

Results and Discussion

With the ligands N-methylimidazole (Nmiz), 1,2-dimethylimidazole (dmiz), and benzimidazole (benziz) two main types of complexes have been obtained: (*i*) complexes with a metal to ligand ratio 1:6, having the formula VL₆X₂ (L = Nmiz, X = I,

BPh₄ = tetraphenylborate) and VL₆X₂·2C₄H₉OH (L = Nmiz, X = Cl, Br); (*ii*) complexes with a metal to ligand ratio 1:4 having the formula VL₄X₂ (L = Nmiz, X = NCS; L = dmiz, X = Cl, Br, NCS; L = benziz, X = Br).

A compound with the formula V(benziz)₂Cl₂·0.5C₄H₉OH has been also obtained.

Finally on heating the green V(Nmiz)₆X₂·2C₄H₉OH complexes under vacuum at a temperature between 80–100 °C, sublimation of the solvent and some ligand molecules takes place yielding violet compounds containing bivalent vanadium. On the basis of elemental analyses the final homogeneous products were assigned formulae V(Nmiz)₄Cl₂ and V(Nmiz)₅Br₂.

Complexes of type *i* in the solid state have proved quite stable toward aerial oxidation, as shown by crystalline samples which, left in the air for several days retained unchanged features of their electronic spectra and magnetic moment values as well as the same colour.

The complexes have effective magnetic moment values at room temperature very close to the spin-only value of 3.87 BM for a d³ configuration. The compound V(benziz)₂Cl₂·0.5C₄H₉OH has a room temperature magnetic moment of 2.41 BM which decreases with temperature (Table II).

Most complexes are soluble in solvents such as acetonitrile, N,N-dimethylformamide, and dichloromethane. In these solvents partial decomposition or oxidation of the complexes takes place, as the absorption spectra appear somewhat different from the solid reflectance spectra.

The ligand-field spectra of the 1:6 derivatives in the solid state are similar to each other and exhibit an intense band at *ca.* 16000 cm⁻¹ and a more or less enhanced shoulder at *ca.* 23000 cm⁻¹. The latter band is partially masked by more intense absorption at higher energy which can be attributed to M→L

TABLE I. Analytical Data for the Complexes.

	Colour	Found %				Calcd %			
		C	H	N	Hal.	C	H	N	Hal.
[V(Nmiz)₆]Cl₂·2C₄H₉OH	Green	49.8	7.50	21.7	9.30	50.50	7.40	22.00	9.31
[V(Nmiz)₆]Br₂·2C₄H₉OH	Green	44.8	6.71	19.9	18.9	45.13	6.63	19.74	18.76
[V(Nmiz)₆]I₂	Green	36.3	4.78	20.8	31.4	36.15	4.48	21.08	31.83
[V(Nmiz)₆](BPh₄)₂	Green	72.8	6.59	14.3		73.15	6.48	14.22	
[V(Nmiz)₄(NCS)₂]	Green	43.2	4.86	28.4		43.62	4.88	28.27	
[V(Nmiz)₄Cl₂]	Violet	43.3	5.75	24.6	16.1	42.69	5.37	24.88	15.75
[V(Nmiz)₅Br]Br	Violet	38.6	4.93	22.3	25.6	38.66	4.86	22.55	25.72
[V(dmiz)₄Cl₂]	Violet	47.3	6.49	22.5	13.8	47.43	6.32	22.12	13.89
[V(dmiz)₄Br₂]	Violet	40.0	5.50	18.8	26.6	40.35	5.42	18.81	26.84
[V(dmiz)₄(NCS)₂]	Green	47.5	5.55	25.6		47.88	5.85	25.39	
[V(benziz)₂Cl₂]·1/2C₄H₉OH	Green	49.0	4.31	14.2	17.6	48.71	4.33	14.17	17.94
[V(benziz)₄Br₂]	Brown	49.5	3.57	16.5	23.1	49.20	3.54	16.40	23.38

TABLE II. Some Physical Data for the Complexes.

Compound	μ_{eff} (BM)[a] (298 K)	State[b]	Absorption Max. $(10^{-3}\ \nu/cm^{-1})$ of the Electronic Spectra, with ϵ_{molar} $(dm^3\ mol^{-1}\ cm^{-1})$ in Parentheses
[V(Nmiz)$_6$]Cl$_2$·2C$_4$H$_9$OH	3.81	R	16.1, 22.8 sh
[V(Nmiz)$_6$]Br$_2$·2C$_4$H$_9$OH	3.81	R	16.1, 22.8 sh
		D	15.0(34), 21.5 sh
[V(Nmiz)$_6$]I$_2$	3.86	R	16.1
		D	15.3(76), 21.7 sh
[V(Nmiz)$_6$](BPh$_4$)$_2$	3.85	R	16.4, 22.3 sh
		D	15.0(36), 21.3sh
[V(Nmiz)$_4$(NCS)$_2$]	3.84	R	16.7, 22.2 sh
[V(Nmiz)$_4$Cl$_2$]	3.86	R	8.5 sh, 15.7 sh, 19.0
		A	15.4 sh, 19.8(1140)
[V(Nmiz)$_5$Br]Br	3.73	R	10.0 sh, 15.0 sh, 19.2
		A	16.1 sh, 19.6(995)
[V(dmiz)$_4$Cl$_2$]	3.87	R	11.3, 15.5, 19.6
[V(dmiz)$_4$Br$_2$]	3.90	R	10.3, 15.8, 19.8
		A	16.4(55), 23.2(75)
[V(dmiz)$_4$(NCS)$_2$]	3.81	R	15.7, 22.2
		C	16.4 sh, 19.4(595)
[V(benziz)$_2$Cl$_2$]·1/2C$_4$H$_9$OH	2.41[c]	R	11.0, 17.1
[V(benziz)$_4$Br$_2$]	3.75	R	10.5, 15.9 sh, 20.5 sh

[a] 1 BM = 9.27×10^{-24} A m^2. [b] R = diffuse reflectance; D = DMF soln.; A = CH$_3$CN soln.; C = CH$_2$Cl$_2$ soln. [c] μ = 1.25 BM at 84 K.

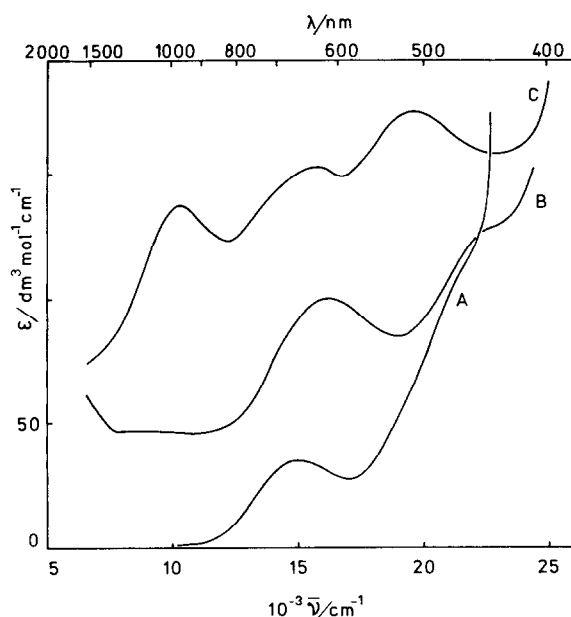Figure 1. Reflectance spectra of [V(Nmiz)$_6$]Br$_2$·2C$_4$H$_9$OH, curve A; [V(dmiz)$_4$Br$_2$], curve C. Absorption spectrum in N,N-dimethylformamide of [V(Nmiz)$_6$]Br$_2$·2C$_4$H$_9$OH, curve B.

charge transfer (Table II and Figure 1). The stoichiometry of the compounds is suggestive of the presence of six-co-ordinate $(VL_6)^{2+}$ cationic species in these compounds.

The quartet terms ^{4}F and ^{4}P arising from the d^3 configuration of the V^{2+} free ion, in a crystal field of O$_h$ symmetry become the ^{4}A$_{2g}$, ^{4}T$_{2g}$, ^{4}T$_{1g}$(F), and ^{4}T$_{1g}$(P) states [5]. The bands at ca. 16000 cm^{-1} and ca. 23000 cm^{-1} can thus be assigned to the first two spin-allowed transitions (^{4}A$_{2g}$→^{4}T$_{2g}$, ν_1; ^{4}A$_{2g}$→^{4}T$_{1g}$(F), ν_2). The third transition (^{4}A$_{2g}$→^{4}T$_{1g}$(P)) is expected at ca. 36500 cm^{-1} [6], and consequently it is outside the spectral range investigated. If these assignments are correct, a value of 1600 cm^{-1} can be derived for the ligand-field strength parameter Dq. Such a value of Dq places Nmiz close to imidazole and pyrazole in the spectrochemical series of the ligands toward vanadium(II) [2a], as also found for other 3d metal complexes [7].

The reflectance spectra of V(dmiz)$_4$X$_2$ (X = Cl, Br) (Table II and Figure 1) significantly differ from those of type *i* complexes as they exhibit a set of three absorption edges in the region between 10000 and 20000 cm^{-1}. These spectra are consistent with a tetragonally distorted *trans* octahedral geometry of the complexes.

The bands at 11300, 15500 cm^{-1} and 10300, 15800 cm^{-1} in the spectra of respectively V(dmiz)$_4$·Cl$_2$ and V(dmiz)$_4$Br$_2$ are tentatively assigned to the transitions ^{4}B$_{1g}$→^{4}E$_g$ and ^{4}B$_{1g}$→^{4}B$_{2g}$. These are the levels in D$_{4h}$ symmetry which derive from the octahedral ^{4}A$_{2g}$ ground state and ^{4}T$_{2g}$ excited state [5]. The band at ca. 20000 cm^{-1} shows no observable splitting and is assigned as a transition to the unresolved components in D$_{4h}$ symmetry of the

second excited state $^4T_{1g}(F)$. The absence of observable splitting of the $^4T_{1g}$ state on lowering the symmetry from O_h to D_{4h} has been also found in most Cr(III) complexes and seems to be due to the ligand-field [8], although hiding of the splitting of the band at 20000 cm^{-1} by the onset of the charge-transfer band cannot be excluded.

The above interpretation of the spectra of the 1:4 vanadium(II) complexes is endorsed by a comparison with the spectra of the 1:6 derivatives. In a tetragonal ligand-field the ground state $^4B_{1g}$ and the second excited state $^4B_{2g}$ differ in energy as much as the ground state $^4A_{2g}$ differs from the first excited state $^4T_{2g}$ in a octahedral field [5, 9]. Therefore the $^4B_{1g} \rightarrow ^4B_{2g}$ (ν_2) transition in the spectra of 1:4 derivatives is expected to occur approximately at the same energy as the $^4A_{2g} \rightarrow ^4T_{2g}$ (ν_1) transition in the spectra of the 1:6 complexes. Furthermore the $^4B_{1g} \rightarrow ^4E_g$ (ν_1) transition should be the most affected on varying the crystal field strength of the axial donor atoms with respect to the in-plane donor atoms. The frequencies of the absorptions of the 1:4 derivatives are in good agreement with the above predictions.

Also the complex V(benziz)$_4$Br$_2$ is assigned a tetragonally distorted six-co-ordinate structure on account of a close similarity of its reflectance spectrum to those of 1:4 dmiz derivatives.

The electronic spectra of VL$_4$(NCS)$_2$ (L = Nmiz, dmiz) do not show the splitting of the low-energy band observed in the spectra of the other 1:4 derivatives (Figure 2), and are indicative of an almost octahedral geometry of the chromophore. The greater

ligand-field strength of thiocyanate ions (N-bonded), which does not differ from that of Nmiz and dmiz as much as that of halide ions, produces a smaller tetragonal distortion and causes the first band (the distortion band) to move to the higher frequency and coalesce with the main band; consequently only a band broadening can be observed in the spectra of thiocyanate derivatives.

The electronic spectrum of V(benziz)$_2$Cl$_2\cdot$0.5C$_4$H$_9$OH is consistent with an essentially octahedral environment around vanadium(II) (Figure 2). The variation of the magnetic moment with temperature also indicates an appreciable antiferromagnetic interaction between metal ions. Both these features suggest a polymeric structure with six-co-ordinate vanadium(II) atoms linked by bridging chlorine atoms and with the ligand molecules presumably *trans* to one another. Not fully consistent with the proposed *trans* octahedral structure is the spectrum of this complex which shows no detectable band splitting, but only a band broadening and a shifting to the lower frequencies, reflecting the relative position of chloride ion with respect to benzimidazole in the spectrochemical series. The essentially octahedral symmetry of the ligand-field in the polymeric V(benziz)$_2$Cl$_2\cdot$0.5C$_4$H$_9$OH derivative can be tentatively rationalized invoking a steric hindrance between benzene ring of the ligand and the equatorial chlorine atoms [11], which forces the nitrogen donor atoms to form longer bonds with the metal ion, thus reducing their effective donor strength.

The coordination geometry of the complexes V(Nmiz)$_4$Cl$_2$ and V(Nmiz)$_5$Br$_2$ is not easily deduced from the spectral evidence available. The electronic spectra of the two complexes are very similar to each other thus indicating that, in spite of the different stoichiometry, vanadium(II) retains essentially the same coordination geometry in both these complexes, but no direct relationship with the spectra of the 1:4 derivatives reported above is apparent (Figure 2). Presumably a large distortion from an idealized tetragonally elongated *trans* octahedral geometry occurs in these complexes owing to a not fully ordered rearrangment of the atoms in the lattice, subsequent the loss of solvent and ligand molecules.

Behaviour in Solution

The hexakis Nmiz derivatives dissolve in N,N-dimethylformamide and V(dmiz)$_4$Br$_2$ in acetonitrile giving light-green solutions. The electronic spectra of the complexes dissolved in the above solvents show two unsplit bands at 15000–16000 and 21000–22000 cm^{-1} thus indicating an essentially octahedral environment around vanadium(II) (Table II and Figure 1). The red shift of the absorption maxima in the spectra of Nmiz derivatives indicates that an at least partial ligand exchange occurs between Nmiz and solvent molecules. The absorption maxima in the
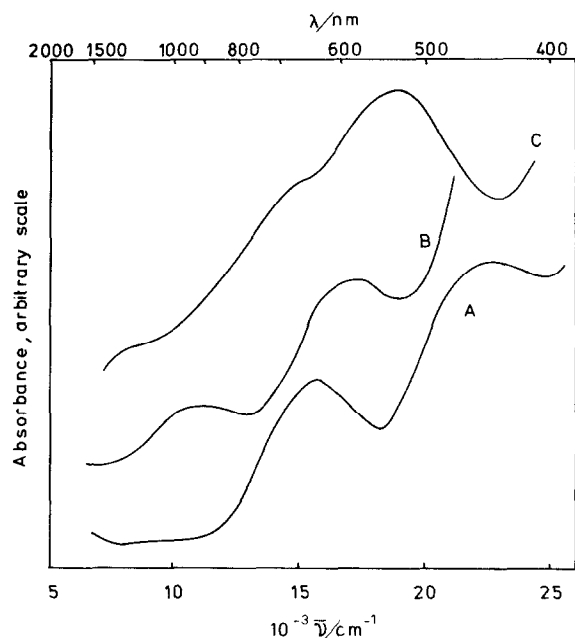

Figure 2. Reflectance spectra of [V(dmiz)$_4$(NCS)$_2$], curve A; [V(benziz)$_2$Cl$_2$]$\cdot$0.5C$_4$H$_9$OH, curve B; [V(Nmiz)$_4$Cl$_2$], curve C.

spectrum of $V(dmiz)_4Br_2$ dissolved in acetonitrile are shifted to higher energy relative to those of the solid reflectance spectrum. Moreover the molar conductivity value 255 cm^2 ohm^{-1} mol^{-1} found for a 10^{-3} molar solution of the complex in the same solvent is in the range expected for a 2:1 electrolyte [12]. Both these facts indicate that almost all the bromide anions are displaced by solvent molecules upon dissolution.

The spectra of dichloromethane or acetonitrile solutions of $V(dmiz)_4(NCS)_2$, $V(Nmiz)_5Br_2$, and $V(Nmiz)_4Cl_2$ show a very intense peak at *ca.* 20000 cm^{-1} with a shoulder at the lower energy side of the main band (Table II). The high-energy bands can be hardly assigned to d–d transitions involving vanadium(II) species as the intensities are very high. On the other hand, the assignment of these bands as due to charge-transfer transitions or to some vanadium(II) and vanadium(III) mixed valencies species does not seem to be fully consistent with the solution spectra of the previously discussed complexes and with the fact that deliberate oxidation of the solutions causes a decrease in the absorbance of the 20000 cm^{-1} peaks.

No physical measurements were possible on the solutions of the other complexes because of their low solubility in the common organic solvents or of the nearly complete decomposition of the solutions, in spite of the care taken to prevent oxidation.

Acknowledgments

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