

## Vanadium(II) Complexes with Macrocyclic Ligands

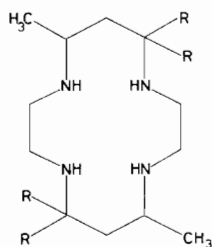
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Coordinating properties of macrocyclic ligands towards most 3d metal ions have been extensively studied also in recent years,<sup>1</sup> but no investigation has been until now undertaken in order to study the donor ability of such ligands towards bivalent vanadium. The ability of some macrocyclic tetramine ligands to stabilize 3d metal ions in their low oxidation states,<sup>2</sup> prompted us to investigate the coordinating behaviour of such ligands also towards vanadium (II) whose coordination chemistry is little known because of the extreme sensitivity of this ion to oxidation by oxygen and water. Among the few examples of vanadium(II) complexes so far reported, only the simple hydrated salts and the complexes with some heterocyclic bases are well characterized.<sup>3</sup>

In this communication we report the synthesis and characterization of some vanadium(II) complexes with the ligands *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane ( $\text{Me}_2[14]\text{aneN}_4$ , I), and *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ( $\text{Me}_6[14]\text{aneN}_4$ , II).



(I), R = H    L =  $\text{Me}_2[14]\text{aneN}_4$

(II), R =  $\text{CH}_3$     L =  $\text{Me}_6[14]\text{aneN}_4$

## Experimental

In order to prevent oxidation, all reactions and operations were carried out under moisture free nitrogen. Vanadium(II) halides,<sup>4</sup>  $\text{Me}_2[14]\text{aneN}_4$  and  $\text{Me}_6[14]\text{aneN}_4$ <sup>5</sup> were prepared as already described. All the complexes, with the exception of  $\text{V}(\text{Me}_6[14]\text{aneN}_4)_2$ , were obtained by the reaction of anhydrous vanadium(II) halides with the appro-

priate ligands using anhydrous dimethylformamide as solvent. The  $\text{V}(\text{Me}_6[14]\text{aneN}_4)_2$  derivative has been obtained in better yield using acetonitrile as solvent. The violet crystalline product thus obtained, which has an analytical formula close to  $\text{V}(\text{Me}_6[14]\text{aneN}_4)_2 \cdot 4\text{CH}_3\text{CN}$ , was heated at ca. 100 °C under vacuum until all the solvent had been lost. Magnetic and spectrophotometric measurements were carried out using methods already described.<sup>6</sup>

## Results and Discussion

The complexes reported here have general formula  $\text{VLX}_2$  (L =  $\text{Me}_2[14]\text{aneN}_4$ , X = Cl; L =  $\text{Me}_6[14]\text{aneN}_4$ , X = Cl, Br, I). All the complexes which are listed in Table I together with their physical data are sensitive to aerial oxidation and atmospheric moisture. The complexes are sparingly soluble in common organic solvents with the exception of dichloromethane and 1,2-dichloroethane. However, in spite of the care employed to prevent oxidation, these solutions decompose in a short time so that physical measurements could not be made.

All the complexes have temperature-independent magnetic moment values close to the spin-only value of 3.87 B.M., as expected for a  $d^3$  configuration.

The ligand field spectra of these vanadium(II) complexes are similar in shape and comparable in frequencies to each other and show at least four more or less well resolved bands in the region 8000–25,000  $\text{cm}^{-1}$  (Table I and Figure 1). The absorptions in the near infrared region are due to overtones of the N–H and C–H stretching frequencies of the ligands.

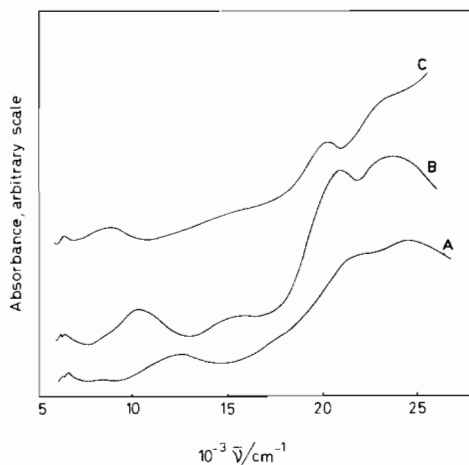


Fig. 1. Reflectance spectra of:  $\text{V}(\text{Me}_6[14]\text{aneN}_4)\text{Cl}_2$ , curve A;  $\text{V}(\text{Me}_6[14]\text{aneN}_4)\text{Br}_2$ , curve B;  $\text{V}(\text{Me}_6[14]\text{aneN}_4)_2$ , curve C.

TABLE I. Analytical and Physical Data for the Complexes.

Compound	Colour	Found %			Calcd. %			$\mu_{\text{eff}}$ , BM (295 K)	Absorption Max., $10^{-3} \bar{\nu}/\text{cm}^{-1}$
		C	H	N	C	H	N		
$\text{V}(\text{Me}_6[14]\text{aneN}_4)\text{Cl}_2$	Light Brown	47.0	9.3	13.6	47.29	8.93	13.79	3.71	12.5; 17.0sh; 22.0; 24.5
$\text{V}(\text{Me}_6[14]\text{aneN}_4)\text{Br}_2$	Light Brown	38.8	7.5	11.5	38.80	7.34	11.31	3.86	10.3; 16.0; 21.0; 23.8
$\text{V}(\text{Me}_6[14]\text{aneN}_4)\text{I}_2$	Pink	32.7	6.2	9.6	32.61	6.16	9.51	3.74	8.5; 15.5sh; 20.0; 24.4sh
$\text{V}(\text{Me}_2[14]\text{aneN}_4)\text{Cl}_2$	Pink	41.3	8.0	15.9	41.15	8.06	16.00	3.73	12.9; 19.2sh; 23.8sh

The electronic spectra can be interpreted assuming a tetragonally distorted octahedral structure of the  $\text{VLX}_2$  complexes. The quadruplet terms  ${}^4\text{F}$  and  ${}^4\text{P}$  arising from the  $d^3$  configuration of the  $\text{V}^{2+}$  free ion give rise in a crystal field of  $\text{O}_h$  symmetry to the  ${}^4\text{A}_{2g}$ ,  ${}^4\text{T}_{2g}$ ,  ${}^4\text{T}_{1g}$  and  ${}^4\text{T}_{1g}(\text{P})$  states. A tetragonal distortion causes the excited states to split into  $\text{E}_g + \text{B}_{2g}$ ,  $\text{A}'_{2g} + \text{E}'_g$  and  $\text{A}''_{2g} + \text{E}''_g$  respectively.<sup>7</sup> On this basis the two bands at lower energies in the spectra of the present complexes are assigned as transitions to the two components in  $\text{D}_{4h}$  symmetry ( ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}'_g$ ;  ${}^4\text{B}_{1g} \rightarrow {}^4\text{B}_{2g}$ ) of the octahedral  ${}^4\text{T}_{2g}$  excited state. The two bands at higher energy are thus assigned as transitions to the components ( ${}^4\text{B}_{1g} \rightarrow {}^4\text{A}'_{2g}$ ;  ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}'_g$ ) in  $\text{D}_{4h}$  symmetry of the second excited state  ${}^4\text{T}_{1g}(\text{F})$ . The expected transitions to the components of the third excited state occur presumably at a higher energy than  $30,000 \text{ cm}^{-1}$  and consequently are outside the spectral range investigated.

It is concluded therefore that in the vanadium(II) complexes reported here the macrocyclic ligands adopt a planar arrangement of the four nitrogen atoms, the halide ions occupying the *trans* axial positions. A strong support to this conclusion comes from the striking similarity of the infrared spectra both in the  $3200\text{--}3000$  and  $1350\text{--}800 \text{ cm}^{-1}$  regions of the present vanadium(II) complexes with those of the other  $3d$  metal complexes with the same ligands, whose *trans* structure has been well established.<sup>1</sup>

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