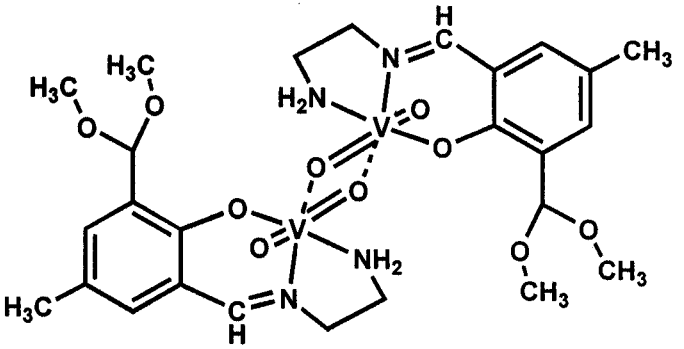
ABSTRACT

Phenolic Schiff base complexes derived from 2,6-diformyl-*p*-cresol with ethane- 1,2 diamine, diethylenetriamine and dipropylenetriamine were investigated because of their potential ability to trap multiple $VO_2^+/VO^{2+}/VO^{3+}$ ions.

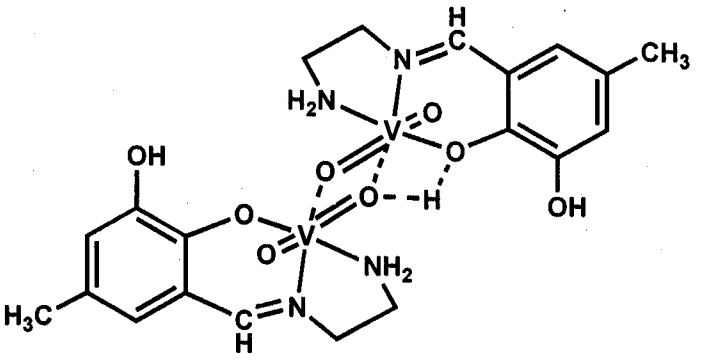
The interaction of VO^{2+} salts with 2,6-diformyl-*p*-cresol and ethane-1,2 diamine yielded an unexpected acetal as a crystalline dinuclear compound of VO_2^+. The crystal structure of **1** reveals the formation of a c_i centrosymmetric $(\mu\text{-O})_2$ oxo-bridged dimeric structure with each Schiff base ligand being tridentate and binding to each vanadium centre via an amine nitrogen, an imine nitrogen and the phenolate oxygen. The coordination at vanadium is distorted octahedral with bond angles at V^{5+} in the ranges 75.7(1) to 106.1(1) and 155.4(1) to 171.8(1) (for the bridging oxygen trans to the terminal oxo). The vanadium (μ-O) distances are asymmetric with V-O (1), 1.675(2) Å and V-O (1'), 2.270(2) Å; the V...V distance is rather short (3.08 Å). The structure of **1** is further stabilized by pairs of intermolecular N-H...O bonds ($N\text{-H}...O_{(phenoxy)}$, 2.12 Å, $N\text{-H-}O_{(terminal\ V = O)}$, 2.10 Å) to form a one-dimensional supramolecular structure along the

crystallographic *b*-axis. Such one-dimensional vanadyl arrays are important as potential conduits for electron transfer in catalysis.



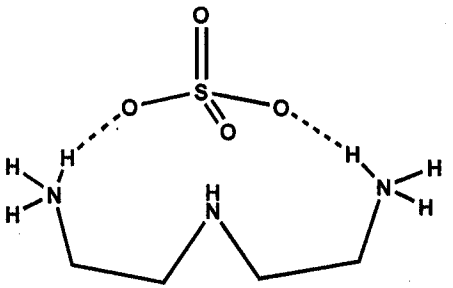
Compound 1

This stable diamagnetic dimeric complex (**1**), when heated to 473 K decomposed to a green paramagnetic product (μ = 1.5 BM) suggesting the formation of a V(V)...V(IV) complex (**2**). EPR spectroscopy of compound **2** revealed an eight line spectrum with coupling constants of A = 99.9 G and a g value of 1.97 which confirms the presence of a vanadyl species.

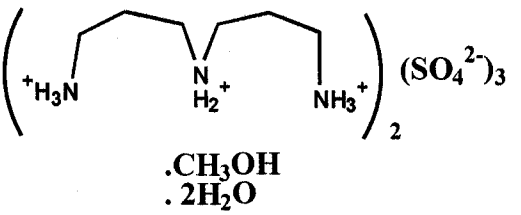


Compound 2

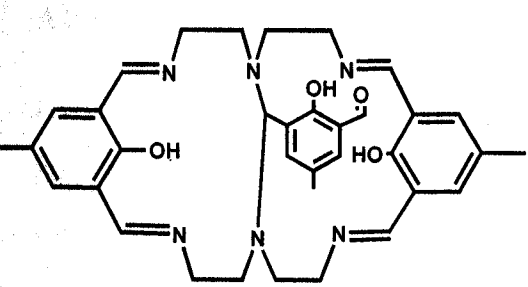
The formation of the two hydrogen bond stabilized hydrolytic amino sulfate products **3** and **6,** as well as two new bicyclic Schiff base ligands **4** and **5** which did not bind vanadyl species, reveal how difficult it is to form dinuclear vanadium macrocyclic complexes.



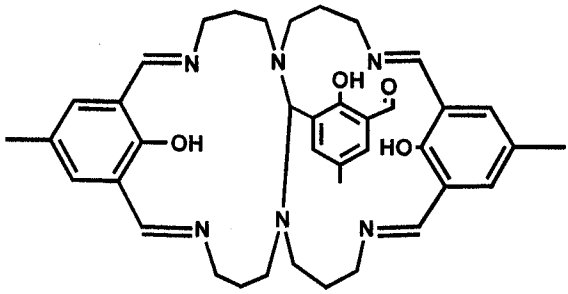
Compound 3



Compound 6

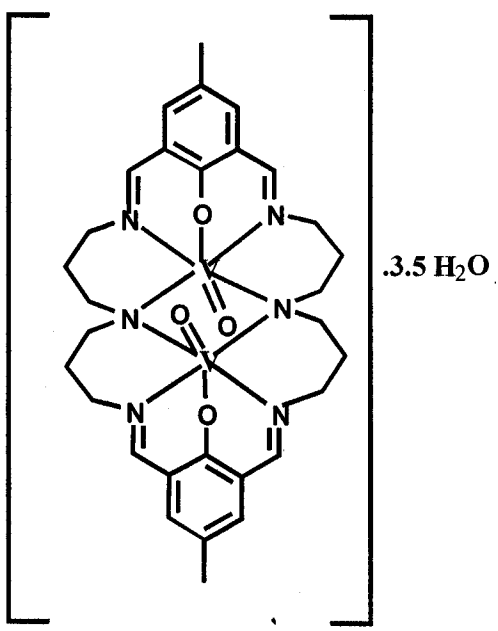


Compound 4



Compound 5

The synthesis of a novel dinuclear vanadium complex $[\mathbf{L}^7(VO)_2.3.5H_2O]$, **7** is reported. EPR spectroscopy of **7** revealed an eight line signal with hyperfine coupling constant of A = 98.3 G in solution. $A_{||}$ = 168.2 G, $A_{\perp}$ = 63.35 G for the axial signal of the solid sample, the isotropic g value is 1.98. The two vanadyl ions in **7** are not interacting. The electron is localized on one of the vanadium centres.



Compound 7