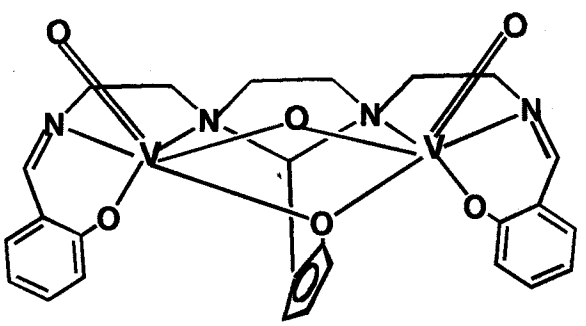
Abstract

Condensation of methanolic salicylaldehyde/ nitrosalicylaldehyde and a series of amines in the presence of vanadyl sulfate produces new vanadium compounds. Compound **11,** formed with triethylenetetramine, is, from structural, magnetic susceptibility, electrochemical and EPR studies a novel mixed valence V(IV/V) compound with unusual electron delocalization on the $[V_2O_3]^{3+}$ core. The crystal structure of **11** reveals the molecule to be in a bent conformation with the vanadyl units (VO) cis to both, each other and the oxo VOV bridge which is very unusual for OVOVO with interacting V(IV)...V(V) systems.



Compound **11**

Compound **12** is the V(V) oxidation/hydrolytic product of **11** and is formed when **11**, in the mother liquor, is exposed to an oxygen atmosphere. Compounds **13-14** are the nitrosalicylaldehyde forms of **11** but illustrate dissimilar electronic behaviour and seem to favour electron localization. Compound **15**, also formed from nitrosalicylaldehyde and triethylenetetramine is a di-vanadium (IV) complex. Compound **16** is a mononuclear vanadium(IV) complex which is formed from a reaction mixture containing tetraethylenepentamine, vanadium sulfate and salicylaldehyde. Its formation is probably due to the break down of the amine by VO^{2+} or by impurities of ethylenediamine in the mixture.

The compounds **17-20** are also mixed valence V(IV/V) complexes formed from the condensation of salicylaldehye and nitrosalicylaldehyde with tetraethylenepentamine and pentaethylenehexamine in the presence of vanadyl sulfate. These complexes however, exhibit behaviour, which suggests isolation of the vanadyl species from each other.

Compounds **21-30** are dendritic polynuclear vanadium complexes. The electronic and magnetic properties of these dendritic compounds show a series of paramagnetic complexes with very dilute magnetic centres.